



Helical phases assembled from achiral molecules: Twist-bend nematic and helical filamentary B_4 phases formed by mesogenic dimers



E. Cruickshank^a, K. Anderson^a, J.M.D. Storey^a, C.T. Imrie^a, E. Gorecka^b, D. Pocięcha^b, A. Makal^b, M.M. Majewska^{b,*}

^a Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, Meston Building, Aberdeen AB24 3UE, UK

^b Faculty of Chemistry, University of Warsaw, ul. Żwirki i Wigury 101, 02-089 Warsaw, Poland

ARTICLE INFO

Article history:

Received 10 September 2021

Revised 19 November 2021

Accepted 21 November 2021

Available online 26 November 2021

Keywords:

Liquid crystals

Nematic phase

Helical nanofilament

B_4 phase

ABSTRACT

The synthesis and characterisation of an homologous series of bent odd-membered mesogenic dimers, the 4'-(6-{4-[(E)-{4-(alkylthio)phenyl}imino)-methyl]phenoxy}hexyl)[1,1'-biphenyl]-4-carbonitriles (CB6O.Sm) is reported. This general class of materials, despite being achiral, has a strong tendency to form helical structures, and here, for the first time we report three such chiral phases in a single homologous series. Specifically, the heliconical twist-bend nematic (N_{TB}) phase for short terminal thioalkyl chains, and its smectic equivalent - the twist-bend smectic C (SmC_{TB}) phase for longer chains. All the dimers showed the helical filament B_4 phase, which is typically seen for rigid bent-core mesogens, but has only rarely been reported for flexible dimeric molecules. In addition, on increasing chain length, smectic behaviour emerges including the smectic A and the smectic C_{TB} phases. We also show that these materials have the potential for their morphology to be controlled through surface interactions. The presence of the little-studied thio-linkage in the terminal chain, and the wide range of properties present in this single group of homologues, with promise of broad applicability in optics, photonics, as well as fundamental significance as a case study to achieve a better understanding of chirality and symmetry breaking in liquid crystals, ensures the importance of this new series of mesogens.

© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

How chirality originates in the absence of a chiral inductor is amongst the most important and topical of scientific questions, cutting across all disciplines, and having clear fundamental and technological relevance (see for example [1]). In this context, liquid crystals provide a wonderful test-bed for studying spontaneous mirror symmetry breaking in fluids [2]. Indeed, the first example of spontaneous mirror symmetry breaking in a fluid with no spatial ordering was the twist-bend nematic, N_{TB} , phase [3–6]. In a conventional nematic phase, the molecules all tend to align in the same direction, known as the director, whereas their centers of mass are randomly distributed. In the N_{TB} phase, the director forms a helix and is tilted with respect to the helical axis (a heliconical structure); the pitch length of the helix is very short, typically ~ 10 nm. *i.e.* just a few molecular lengths. The formation of chirality is spontaneous and so equal numbers of left- and right-handed helices are expected and overall, the system is racemic. This degen-

eracy may be removed by the introduction of intrinsic molecular chirality, leading to the N_{TB}^* phase [7]. The vast majority of materials that show the N_{TB} phase may be described as odd-membered dimers, in which two mesogenic units are attached by a flexible spacer containing an odd number of atoms, and such molecules have a bent molecular shape [8–11], however this phase has also been observed for rigid bent-core mesogens [12] as well as for oligomers including both, linear and bent-core segments [13]. Recently it was shown that odd-membered dimers not only exhibit the N_{TB} phase but also show twist-bend smectic phases [14–17]. In these fascinating heliconical lamellar phases consisting of achiral molecules up to four levels of structural chirality were observed: layer chirality, helicity of a basic repeating unit, a mesoscopic helix and helical filaments. Another phase with a spontaneously chiral structure built of achiral molecules is the helical nanofilament phase (HNF, B_4), most commonly observed for rigid bent core mesogens [18,19] and only rarely for bent dimers [20].

In our search for new examples of chiral systems made of achiral building blocks, here we report the synthesis and characterization of non-symmetric dimeric mesogens consisting of a cyanobiphenyl core, an odd-membered spacer and a benzylidene

* Corresponding author.

E-mail address: mmajewska@chem.uw.edu.pl (M.M. Majewska).

aniline unit terminated with an alkylthio chain, the 4'-(6-{4-[(E)-{4-(alkylthio)phenyl}imino]-methyl]phenoxy}hexyl)[1,1'-biphenyl]-4-carbonitriles (Fig. 1) and refer to them using the acronym CB6O.Sm, in which m denotes the number of carbon atoms in the terminal chain. The flexible hexyloxy spacer linking the two mesogenic units contains seven atoms, and ensures the necessary molecular curvature required for twist-bend phases to be observed [21,22]. Liquid crystals with terminal alkylthio chains are extremely topical due to their high values of birefringence arising from the polarisable sulfur atom [23–25]. Highly birefringent nematogens have the potential not only to improve liquid crystal display technology, but also have an important role to play in emerging fields such as liquid crystal lasers and lenses [26,27]. Fundamentally, the introduction of the thio linkage is providing a demanding challenge to our understanding of the relationships between molecular structure and liquid crystalline behaviour [28–31].

The CB6O.Sm series exhibits a rich range of phase behaviour depending on the length of the terminal chain including twist-bend phases, and the B₄ phase [18,19] at room temperature, a crystalline phase with an unusual morphology of twisted filaments. The properties of the CB6O.Sm series are compared to those of the analogous materials having alkyl CB6O.m [32] and alkyloxy CB6O.Om [33] terminal chains.

2. Experimental section

2.1. Synthesis

The synthetic route used to prepare the CB6O.Sm series is shown in Scheme S11 in the ESI along with detailed descriptions of their synthesis, including the structural characterization data for all intermediate and final products.

2.2. Methods

The phase behaviour of the CB6O.Sm series was studied by differential scanning calorimetry (DSC) using a Mettler Toledo DSC1 calorimeter equipped with a TSO 801RO sample robot and calibrated using indium and zinc standards. The optical studies of the phases were conducted using a Zeiss Axio Imager A2m polarised light microscope with a Linkam heating stage. The samples were placed either between two untreated thin glass slides or in glass cells with planar anchoring induced by a thin inner layer of polymer. The cells were filled by capillary action with the material in the isotropic phase. Birefringence was measured using a setup based on a photoelastic modulator (PEM-90, Hinds) working at a modulation $f = 50$ kHz; as a light source a halogen lamp (Hamamatsu LC8) was used, equipped with a narrow band pass filter (532 nm). The transmitted light intensity was measured with a photodiode (FLC Electronics PIN-20) and deconvoluted with a lock-in amplifier (EG&G 7265) into $1f$ and $2f$ components to yield a retardation induced by the sample. The dielectric permittivity was measured using a Wayne Kerr Precision Component Analyzer 6425, at the frequency 12 kHz, and with the applied voltage amplitude (V) ranging from 0.1 to 5.0 V. The splay elastic constant K_{11} was determined from the threshold voltage V_{th} at which the director reorientation starts, and thus the effective permittivity (ϵ) starts to grow as: $K_{11} = \Delta\epsilon\epsilon_0 \left(\frac{V_{th}^2}{\pi^2}\right)$. The bend elastic constant, K_{33}

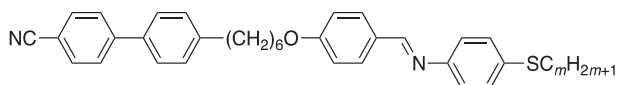


Fig. 1. Chemical structure of the CB6O.Sm series, $m = 1-13, 15, 17, 18, 22$.

was estimated by fitting the $\epsilon(V)$ dependence far above the threshold voltage using [34]:

$$\frac{\epsilon(V) - \epsilon_{\perp}}{\epsilon_{\parallel} - \epsilon_{\perp}} = 1 - \frac{2}{\pi} \sqrt{1 + \xi} \frac{V_{th}}{V} \int_0^1 \sqrt{\frac{1 + \kappa x^2}{1 + \xi x^2}} dx$$

where $\xi = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\perp}}$ and $\kappa = \frac{K_{33} - K_{11}}{K_{11}}$.

For X-ray measurements three different set-ups were used, the Bruker D8 Discover, Bruker GADDS and Bruker Nanostar systems, all using CuK α radiation, $\lambda = 1.54$ Å. The samples for these measurements were prepared in the form of a thin film or a droplet on a heated surface. For AFM measurements, a Bruker Dimension Icon Microscope was used in tapping or scan assist mode. The cantilevers with elastic constant of 0.4 N/cm² were applied. The SEM measurements were performed using a FE-SEM Zeiss Merlin electron microscope operating at 5 keV utilizing an in-lens detector of secondary electrons. Samples were sputter coated with gold and palladium before imaging. To align the B₄ phase, the material was filled into porous anodic aluminium oxide (AAO) with a 60 nm pore size provided by Prof. Dong Ki Yoon's group from the Korea Advanced Institute of Science and Technology; the nanoconfinement prompted the formation of highly ordered nanostructures [35]. The CD spectra were recorded using a Chirascan Plus Applied Photophysics spectrometer. Samples with large domains of B₄ crystals were grown by placing material on a quartz slide, heating it to the isotropic liquid and cooling to room temperature.

3. Results and discussion

The phase transition temperatures and associated scaled entropy changes for the CB6O.Sm series are given in Table S1 in ESI. The dependence of the transition temperatures on the length of the terminal alkylthio chain m is shown in Fig. 2. The homologues with $m = 1-11$ show the conventional nematic phase and, the twist-bend nematic phase below, apart from compounds $m = 9$ and $m = 10$, the observed mesophases are monotropic. For CB6O.S3 crystallization precluded the observation of the N_{TB} phase, and a virtual N-N_{TB} transition temperature was estimated from a phase diagram constructed using binary mixtures of CB6O.S3 and CB7CB [6]. The longer homologues, $m \geq 12$, showed smectic phases below the nematic phase.

The N - N_{TB} phase transition was accompanied by the appearance of the characteristic stripe texture (Fig. 3(a) and (b)), that is formed due to the pseudo-layer undulation in a confined cell

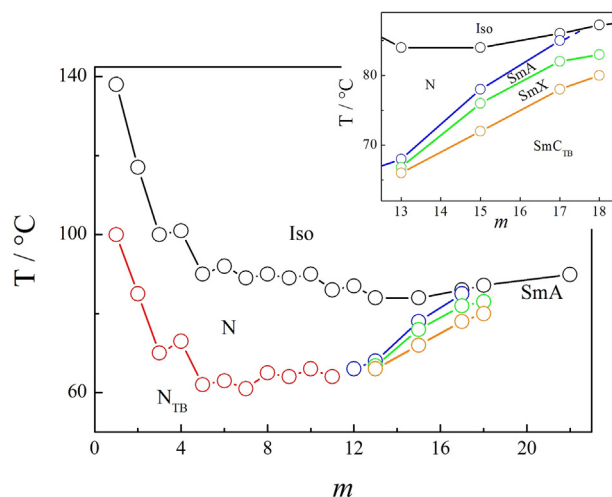


Fig. 2. The dependence of the transition temperatures on the length of the terminal alkylthio chain, m , for the CB6O.Sm series, the temperatures were registered on cooling. The inset shows an expanded region of the phase diagram for $m = 13-18$.

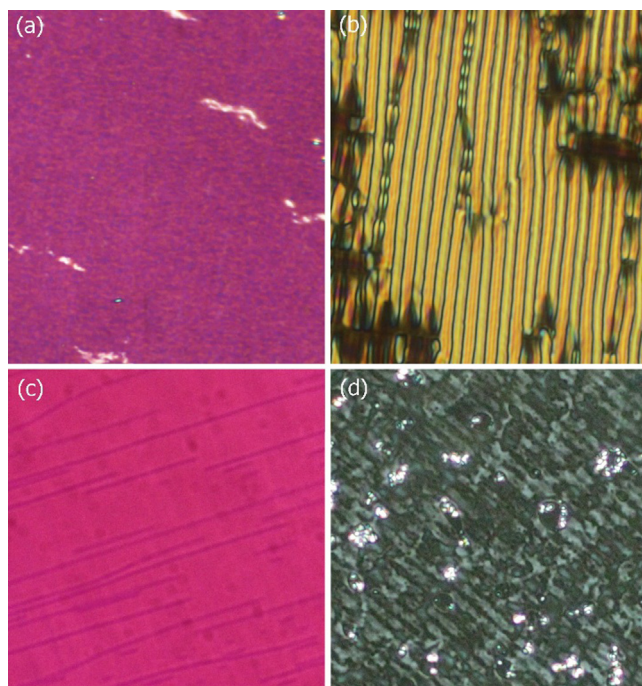


Fig. 3. Optical textures of the (a) N phase and (b) N_{TB} phase for CB60.S9 observed in a 1.6- μm thick planar cell. Textures of the SmX phase for CB60.S18 observed in (c) a 1.6- μm thick planar cell and (d) a cell with homeotropic anchoring. In an homeotropic cell the SmX phase forms a texture with a regular array of stripes. Thin darker lines visible in panel (c) are the regions of slightly higher birefringence.

geometry [36]. The X-ray patterns of the nematic and twist-bend nematic phases are almost indistinguishable. In the low diffraction angle range, despite the presence of the heavy sulfur atom in the molecular structure, there are broad signals of very weak intensity as also seen for the corresponding dimers having alkoxy terminal chains, the CB60.O m series [33]. For the short homologues, the low angle diffraction signal corresponds to half the molecular length, and on increasing the terminal chain length a signal related to the full molecular length appears and grows in intensity (Fig. 4). For the longest homologues, the X-ray diffraction pattern of the nematic phase contains a signal corresponding to twice the molecular length, which on cooling narrows and becomes apparatus-resolution limited in the smectic phase. This indicates that the smectic phases have a repeating structural unit composed of a molecular bilayer.

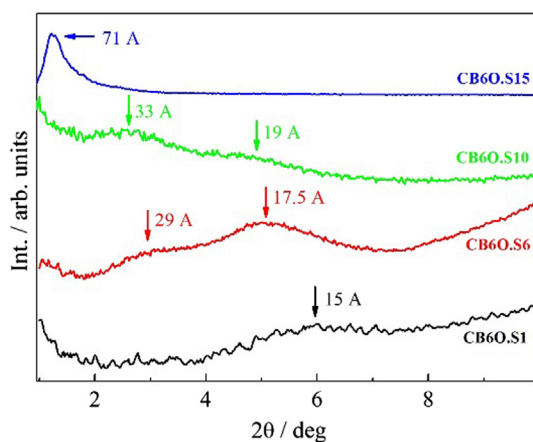


Fig. 4. Low angle X-ray diffraction patterns recorded in the nematic phase of CB60. Sm homologues with different lengths of terminal chain. Real space distances corresponding to the signal positions are indicated.

Formation of the N_{TB} phase, in which the molecules are tilted with respect to the helical axis, is accompanied by a deviation of the optical birefringence, Δn , from its power law temperature dependence observed in the nematic phase (Fig. 5). By analyzing the Δn decrease, the conical angle in the twist-bend nematic phase was determined according to the procedure described by Meyer et al. [37] to be ~ 20 deg. far from the N - N_{TB} transition. Interestingly, the measured optical birefringence starts to deviate from the power law dependence several degrees above the N - N_{TB} transition temperature, and this has been attributed to pretransitional fluctuations, specifically the formation of an instantaneous helical structure in the N phase [38].

The value of the optical birefringence expected for the nematic phase with ideal orientational order, $S = 1$, Δn_{max} , decreases on increasing the length of the terminal chain; for CB60.S9 $\Delta n_{max} = 0.355$ and for CB60.S17, $\Delta n_{max} = 0.302$. This decrease may be attributed to the reduction in the polarizability anisotropy of the molecule on changing the ratio between the strongly anisotropic mesogenic cores and the less anisotropic alkyl chains. The static dielectric anisotropy, $\Delta\epsilon$, in the nematic phase is small and positive (Fig. S8). This implies that the dimers are locally arranged head-to-head, such that the longitudinal dipole moments associated with the cyano groups are almost compensated. The bend elastic constant is smaller than the splay elastic constant, $K_{33} < K_{11}$, over almost the entire temperature range of the nematic phase (Fig. S8), and this is typical behavior for bent dimers [34]. K_{33} decreases strongly upon approaching the twist-bend nematic phase whereas K_{11} increases monotonically with decreasing temperature and increasing order parameter.

For the longer homologues, a smectic A phase was formed on cooling the nematic phase ($m = 12, 13, 15, 17$) or directly from the isotropic liquid ($m = 18, 22$). In planar cells no change of the extinction direction upon the transition from the nematic to smectic A phase was found, the optical axis remains along the rubbing direction and only a small increase of the birefringence was detected (Fig. 5), revealing that the smectic phase is orthogonal. In one-free-surface samples, a homeotropic texture was found, confirming the optical uniaxiality of the smectic A phase (Fig. 6). For dimers with $m = 13$ –18, below the narrow temperature range of the SmA phase, two additional smectic phases were observed, the upper one (SmX) exhibiting a birefringent texture and the lower (Sm $_{CTB}$) a homeotropic texture (Fig. 6) in one-surface-free samples. In a wedge cell with homeotropic anchoring, the upper

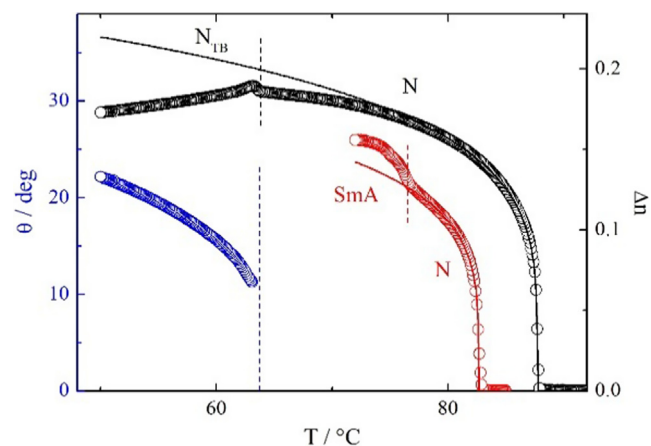


Fig. 5. Optical birefringence of CB60.S9 (black circles) and CB60.S17 (red circles). Lines show the power law temperature dependence $\Delta n = \Delta n_{max} \left(\frac{T_c - T}{T_c}\right)^\beta$, with Δn_{max} being 0.355 and 0.302 for CB60.S9 and CB60.S17, respectively, and critical exponent $\beta = 0.21$ for both compounds. The decrease in the measured birefringence in the N_{TB} phase of compound CB60.S9 allowed for the determination of the helical tilt angle, θ (blue circles).

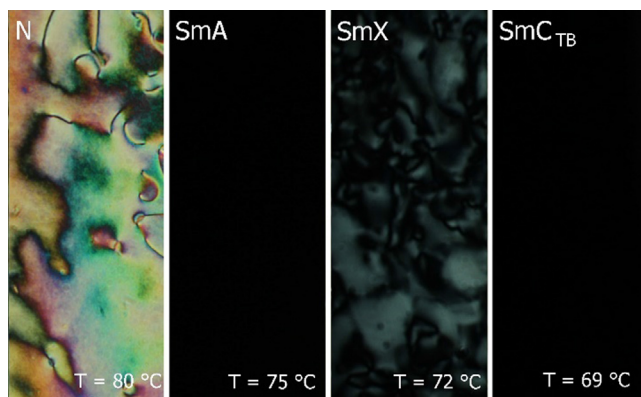


Fig. 6. Optical textures observed on cooling a one-free-surface sample of CB60.S15.

phase texture is decorated with dynamically moving stripes (Fig. 3d), such a texture was ascribed to the biaxial smectic A phase, SmA_b [39], an orthogonal smectic phase in which molecular rotation around the long axis is restricted. However, the birefringent texture of the SmX phase could also evidence a tilted SmC-like structure.

In a planar cell, careful observation of the SmX phase texture revealed the presence of lines on a uniform background (Fig. 3c), associated with regions of slightly higher birefringence. To determine whether SmX is an orthogonal SmA_b phase or tilted SmC phase we performed an experiment with doping the CB60.S15 compound with small amount of chiral additive. As a result the SmX became optically uniaxial, giving perfect homeotropic texture. We concluded therefore that the SmX phase is tilted SmC-like phase, because the chiral doping promoted a helix formation and consequently the uniaxiality of the phase. The SmA_b phase would have been insensitive to chirality [40]. A similar phase sequence and associated textural changes were found for the CB60.m series [41], suggesting that both tilted phases observed below SmA phase have heliconical structure (SmC_{TB} -type). However, the monotropic nature of all the smectic phases and rapid recrystallization precluded their detailed characterization.

Interestingly, when cooled rapidly in thin cells, all the dimers studied recrystallized into the B_4 phase ('blue crystal'), the characteristic feature of which is a twisted ribbon morphology [19]. It should be pointed out, however, that whereas for the longer homologues the B_4 crystal was stable at room temperature for months, the shorter homologues often displayed 'blue' crystals coexisting with other strongly birefringent crystalline phases and heating the sample resulted in a polymorphic transition from the metastable B_4 phase to the birefringent crystal. In calorimetric measurements B_4 phase was detected regardless of applied cooling rate ($1-50 \text{ K min}^{-1}$), its formation was accompanied by enthalpy change of order of 50 kJ mol^{-1} . On heating, B_4 phase undergoes exothermic transition into another crystalline phase. The lamellar character of the B_4 phase was confirmed by X-ray diffraction studies (Fig. S1). The periodicity of the layered structure was found to be close to twice the molecular length, showing that the molecules are arranged in an antiparallel fashion in consecutive layers. The width of the diffraction signals was considerably broader than the instrumental resolution, and this is attributed to the limited width of the ribbons forming the helical filaments [20]. The B_4 phase showed a weakly birefringent (due to the not completely random orientation of the molecular layers), but an optically active texture (Fig. 7), and domains with opposite signs of the optical rotation were formed with equal probability. Given that these domains could be grown with dimensions comparable to the sample size, it was possible to prepare samples having a strong imbal-

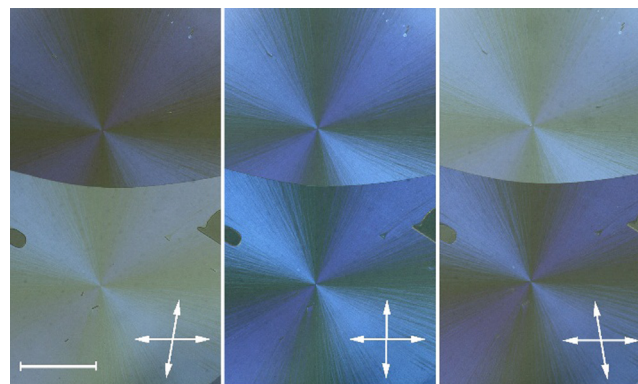


Fig. 7. Weakly birefringent, optically active domains of the B_4 phase of CB60.S15, observed between crossed and slightly de-crossed (by 3 deg.) polarizers. Scale bar corresponds to 200 μm .

ance between opposite chirality domains enabling the measurement of circular dichroism (CD) spectra, see Fig. 8, and Figs S2 and S3 in the ESI. A strong CD signal was observed at the wavelength of the absorption edge of the compound in the solid state, $\sim 400 \text{ nm}$ (Fig. S2).

In order to correlate the optical rotatory power (ORP) and CD signal with the structure/morphology of the B_4 phase, the almost homochiral sample was further studied using AFM, which revealed membranes made of molecular layers with a number of strongly saddle-splay deformed areas randomly distributed in space (Fig. 9), resembling the morphology of the dark conglomerate phase [42]. No areas with clear helical filaments could be seen. The almost random distribution of the layer orientation is consistent with the low optical birefringence of the sample. The absence of a clear helical morphology also suggests that the chiral nature of the phase, which gives rise to optical activity, originates from the layer chirality [43] rather than from a helical morphology. To obtain more information about the phase morphology, the sample was aligned using porous anodic aluminium oxide (AAO) and imaged with SEM, and under such conditions helical twisted ribbons, with a helical pitch of $\sim 120 \text{ nm}$, were observed (Fig. 9). Apparently, the morphology of the sample, i.e. filaments vs dark conglomerate phase, may be controlled, at least to some extent, by surface interactions, despite the crystalline nature of the phase. It has been recently reported [44] that limiting space for the nucleation of saddle-splay deformed layers promotes the formation of helical filaments growing along the AAO channel axis over

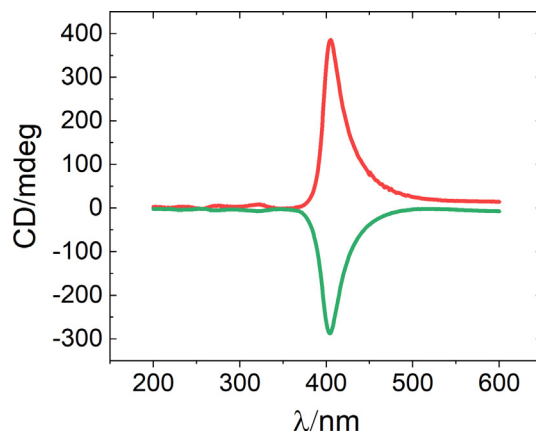


Fig. 8. CD spectra for two samples of CB60.S18, with opposite chirality macroscopic domains of the B_4 crystal phase, thin films measured on quartz.

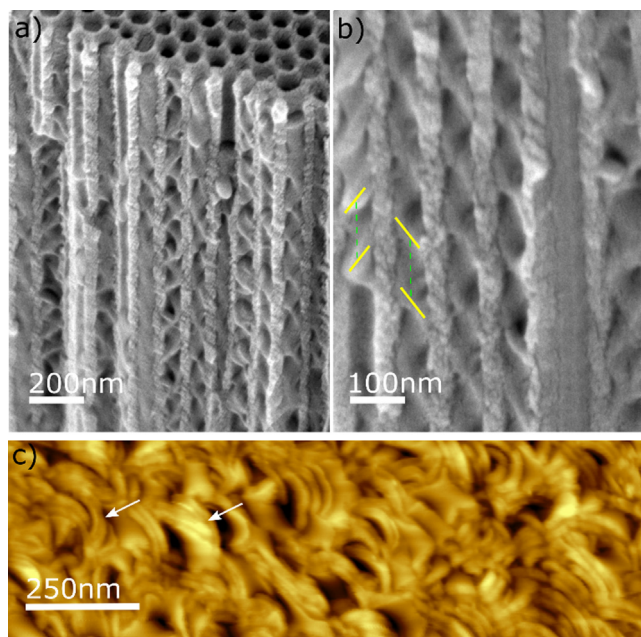


Fig. 9. (a, b) SEM images of helical filaments of B_4 phase of CB60.S17 grown in an AAO template, each pore of the template has a 60 nm diameter, the pitch of both right- and left-handed filaments is approximately 120 nm. (c) AFM height image of the B_4 phase of CB60.S18 on quartz, the randomly distributed strongly deformed membranes made of molecular layers (marked with arrows) are visible.

the formation of the 3-dimensional deformed dark conglomerate structures.

Comparing the thioalkyl CB60.Sm dimers studied here with the corresponding alkyloxy CB60.Om [33] and alkyl CB60.m series [32,41] reveals that the N-Iso transition temperatures, T_{NI} , are lowest for the mesogens having an alkylthio chain and highest for those with an alkyloxy chain. This may be attributed to the changes of bond angle between the mesogenic unit and the terminal chain, and the position of the chain with respect to the plane of the mesogenic unit. Thus, an alkyloxy chain lies more or less in the plane of the mesogenic core whereas the alkylthio and alkyl chains protrude at some angle. In addition, C-S-C is the smallest of the three bond angles and this reduces the overall molecular shape anisotropy. The exceptions to this behavior are CB60.S1 and CB60.S2, for which the isotropisation temperatures are considerably higher than expected. It has been suggested that this may be attributed to chalcogen bonding in these compounds [45]. Although such an interaction cannot be excluded in the liquid crystalline state, our X-ray diffraction studies show no direct S-S contact interactions in the crystalline state, while crystal packing appeared to maximize the amount of C-H...S interactions (Fig. S3-S6). Although the N-Iso transition temperatures of the CB60.Sm series tend to be lower, their melting points are higher than for the corresponding alkyl and alkyloxy series, resulting in the monotropic nature of the liquid crystalline phases that have a strong tendency to crystallize, this behavior can be attributed to presence of relatively strong C-H...S interactions (see SI). All three series, CB60.Sm, CB60.Om and CB60.m, show bilayer structures for long terminal chains, and intercalated structures for the shorter chains, with a gradual evolution of the molecular packing as the terminal chain length is changed. It should be stressed that for all three series, smectic phases were observed; for the CB60.Sm series for $m \geq 13$ and for CB60.m series for $m \geq 10$. By comparison, the CB60.Om series shows smectic behaviour only for intermediate length compounds, with $m = 3, 4$ and 5 [33]. The observation of smectic phase behavior for intermediate chain lengths only in the CB60.Om series is thought to be related to the ability of these

dimers to better pack into an intercalated structure, and this arises from both the alkyloxy chain lying in the plane of the benzylidene-aniline unit and the larger C-O-C bond angle compared to C-S-C.

4. Conclusions

We report the first series of flexible mesogenic dimers for which N_{TB} and B_4 phases are observed for a single compound as a function of temperature. Although the N_{TB} phase is relatively common in bent, flexible dimers, the formation of the B_4 phase for such molecules is unusual [20,46], this phase is normally observed for rigid bent core molecules [18,19,47]. The dimers reported here also form another type of helical phases, SmC_{TB} -type, which is the smectic analogue of the N_{TB} phase. Unfortunately, the monotropic nature of the smectic phases precluded their further investigation.

Funding

National Science Centre (Poland) under the grant no. 2016/22/A/ST5/00319.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The work was financed by the National Science Centre (Poland) under the grant no. 2016/22/A/ST5/00319. Special acknowledgment and thanks to professor Dong Ki Yoon's group for providing the AAO membranes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.118180>.

References

- [1] T. Buhse, J.-M. Cruz, M.E. Noble-Terán, D. Hochberg, J.M. Ribó, J. Crusats, J.-C. Micheau, Spontaneous deracemizations, *Chem. Rev.* 121 (4) (2021) 2147–2229, <https://doi.org/10.1021/acs.chemrev.0c00819>.
- [2] C. Tschierske, Mirror symmetry breaking in liquids and liquid crystals, *Liq. Cryst.* 45 (13–15) (2018) 2221–2252, <https://doi.org/10.1080/02678292.2018.1501822>.
- [3] I. Dozov, On the spontaneous symmetry breaking in the mesophases of achiral banana-shaped molecules, *Europhys. Lett.* 56 (2) (2001) 247–253, <https://doi.org/10.1209/epl/i2001-00513-x>.
- [4] V. Borshch, Y.K. Kim, J. Xiang, M. Gao, A. Jáklí, V.P. Panov, J.K. Vij, C.T. Imrie, M. G. Tamba, G.H. Mehl, O.D. Lavrentovich, Nematic twist-bend phase with nanoscale modulation of molecular orientation, *Nat. Commun.* 4 (2013) 2635, <https://doi.org/10.1038/ncomms3635>.
- [5] D. Chen, J.H. Porada, J.B. Hooper, A. Klitnick, Y. Shen, M.R. Tuchband, E. Korblova, D. Bedrov, D.M. Walba, M.A. Glaser, J.E. MacLennan, N.A. Clark, Chiral heliconic ground state of nanoscale pitch in a nematic liquid crystal of achiral molecular dimers, *Proc. Natl. Acad. Sci. U. S. A.* 110 (40) (2013) 15931–15936, <https://doi.org/10.1073/pnas.1314654110>.
- [6] 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, H. Zimmermann, Phase behavior and properties of the liquid-crystal dimer 1',7''-bis(4-cyanobiphenyl-4'-yl) heptane: a twist-bend nematic liquid crystal, *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* 84 (2011) 31704, <https://doi.org/10.1103/PhysRevE.84.031704>.
- [7] R. Walker, D. Pocięcha, J.M.D. Storey, E. Gorecka, C.T. Imrie, The chiral twist-bend nematic phase (N^*TB), *Chem. - A Eur. J.* 25 (58) (2019) 13329–13335, <https://doi.org/10.1002/chem.201903014>.
- [8] R.J. Mandle, C.T. Archbold, J.P. Sarju, J.L. Andrews, J.W. Goodby, The dependency of nematic and twist-bend mesophase formation on bend angle, *Sci. Rep.* 6 (2016) 1–12, <https://doi.org/10.1038/srep36682>.
- [9] E. Forsyth, D.A. Paterson, E. Cruickshank, G.J. Strachan, E. Gorecka, R. Walker, J. M.D. Storey, C.T. Imrie, Liquid crystal dimers and the twist-bend nematic

- phase: on the role of spacers and terminal alkyl chains, *J. Mol. Liq.* 320 (2020) 114391, <https://doi.org/10.1016/j.molliq.2020.114391>.
- [10] R. Walker, M. Majewska, D. Pocięcha, A. Makal, J.M. Storey, E. Gorecka, C.T. Imrie, Twist-bend nematic glasses: the synthesis and characterisation of pyrene-based nonsymmetric dimers, *ChemPhysChem*. 22 (2021) 461–470, <https://doi.org/10.1002/cphc.202000993>.
- [11] Y. Arakawa, K. Komatsu, S. Inui, H. Tsuji, Thioether-linked liquid crystal dimers and trimers: the twist-bend nematic phase, *J. Mol. Struct.* 1199 (2020) 126913, <https://doi.org/10.1016/j.molstruc.2019.126913>.
- [12] D. Chen, M. Nakata, R. Shao, M.R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D.M. Walba, M.A. Glaser, J.E. MacLennan, N.A. Clark, Twist-bend heliconical chiral nematic liquid crystal phase of an achiral rigid bent-core mesogen, *Phys. Rev. E*. 89 (2014) 22506, <https://doi.org/10.1103/PhysRevE.89.022506>.
- [13] Y. Wang, G. Singh, D.M. Agra-Kooijman, M. Gao, H.K. Bisoyi, C. Xue, M.R. Fisch, S. Kumar, Q. Li, Room temperature heliconical twist-bend nematic liquid crystal, *CrystEngComm*. 17 (14) (2015) 2778–2782, <https://doi.org/10.1039/C4CE02502D>.
- [14] S.P. Sreenilayam, Y.P. Panarin, J.K. Vij, V.P. Panov, A. Lehmann, M. Poppe, M. Prehm, C. Tschierske, Spontaneous helix formation in non-chiral bent-core liquid crystals with fast linear electro-optic effect, *Nat. Commun.* 71 (7) (2016) 1–8, <https://doi.org/10.1038/ncomms11369>.
- [15] J.P. Abberley, R. Killah, R. Walker, J.M.D. Storey, C.T. Imrie, M. Salamończyk, C. Zhu, E. Gorecka, D. Pocięcha, Heliconical smectic phases formed by achiral molecules, *Nat. Commun.* 9 (2018) 228, <https://doi.org/10.1038/s41467-017-02626-6>.
- [16] M. Salamończyk, N. Vaupotič, D. Pocięcha, R. Walker, J.M.D. Storey, C.T. Imrie, C. Wang, C. Zhu, E. Gorecka, Multi-level chirality in liquid crystals formed by achiral molecules, *Nat. Commun.* 10 (2019) 1922, <https://doi.org/10.1038/s41467-019-09862-y>.
- [17] J.K. Vij, Y.P. Panarin, S.P. Sreenilayam, M. Alaasar, C. Tschierske, Investigation of the heliconical smectic $\langle \text{math} \rangle$ phases, *Phys. Rev. Mater.* 3 (2019) 045603, <https://doi.org/10.1103/PhysRevMaterials.3.045603>.
- [18] T. Sekine, T. Niiri, J. Watanabe, T. Furukawa, S.W. Choi, H. Takezoe, Spontaneous helix formation in smectic liquid crystals comprising achiral molecules, *J. Mater. Chem.* 7 (1997) 1307–1309, <https://doi.org/10.1039/A702026K>.
- [19] L.E. Hough, H.T. Jung, D. Krüerke, M.S. Heberling, M. Nakata, C.D. Jones, D. Chen, D.R. Link, J. Zasadzinski, G. Heppke, J.P. Rabe, W. Stocker, E. Korblova, D. M. Walba, M.A. Glaser, N.A. Clark, Helical nanofilament phases, *Science*. 325 (5939) (2009) 456–460.
- [20] E. Bialecka-Florjańczyk, I. Ślędzka, E. Górecka, J. Przedmojski, Odd-even effect in biphenyl-based symmetrical dimers with methylene spacer – evidence of the B4 phase, *Liq. Cryst.* 35 (4) (2008) 401–406, <https://doi.org/10.1080/02678290801906052>.
- [21] D.A. Paterson, M. Gao, Y.K. Kim, A. Jamali, K.L. Finley, B. Robles-Hernández, S. Diez-Berart, J. Salud, M.R. De La Fuente, B.A. Timimi, H. Zimmermann, C. Greco, A. Ferrarini, J.M.D. Storey, D.O. López, O.D. Lavrentovich, G.R. Luckhurst, C.T. Imrie, Understanding the twist-bend nematic phase: the characterisation of 1-(4-cyanobiphenyl-4'-yloxy)-6-(4-cyanobiphenyl-4'-yl)hexane (CB6OCB) and comparison with CB7CB, *Soft Matter*. 12 (2016) 6827–6840, <https://doi.org/10.1039/c6sm00537c>.
- [22] D.A. Paterson, R. Walker, J.P. Abberley, J. Forestier, W.T.A. Harrison, J.M.D. Storey, D. Pocięcha, E. Gorecka, C.T. Imrie, Azobenzene-based liquid crystal dimers and the twist-bend nematic phase, *Liq. Cryst.* 44 (2017) 2060–2078, <https://doi.org/10.1080/02678292.2017.1366075>.
- [23] Y. Arakawa, S. Inui, K. Igawa, H. Tsuji, Alkylthio- and alkyl-substituted asymmetric diphenyldiacetylene-based liquid crystals: phase transitions, mesophase and single-crystal structures, and birefringence, *Liq. Cryst.* 46 (2019) 1621–1630, <https://doi.org/10.1080/02678292.2019.1590744>.
- [24] Y. Arakawa, Y. Sasaki, N. Haraguchi, S. Itsuno, H. Tsuji, Synthesis, phase transitions and birefringence of novel liquid crystalline 1,4-phenylene bis(4-alkylthio benzoates) and insights into the cybotactic nematic behaviour, *Liq. Cryst.* 45 (6) (2018) 821–830, <https://doi.org/10.1080/02678292.2017.1385103>.
- [25] Y. Arakawa, S. Kang, H. Tsuji, J. Watanabe, G.-I. Konishi, Development of novel bistolane-based liquid crystalline molecules with an alkylsulfanyl group for highly birefringent materials, *RSC Adv.* 6 (20) (2016) 16568–16574.
- [26] J. Xiang, A. Varanytsia, F. Minkowski, D.A. Paterson, J.M.D. Storey, C.T. Imrie, O.D. Lavrentovich, P. Palffy-Muhoray, Electrically tunable laser based on oblique heliconical cholesteric liquid crystal, *Proc. Natl. Acad. Sci. U. S. A.* 113 (46) (2016) 12925–12928, <https://doi.org/10.1073/pnas.1612212113>.
- [27] J. Xiang, Y. Li, Q. Li, D.A. Paterson, J.M.D. Storey, C.T. Imrie, O.D. Lavrentovich, Electrically tunable selective reflection of light from ultraviolet to visible and infrared by heliconical cholesterics, *Adv. Mater.* 27 (19) (2015) 3014–3018, <https://doi.org/10.1002/adma.201500340>.
- [28] Y. Arakawa, Y. Ishida, H. Tsuji, Ether- and thioether-linked naphthalene-based liquid-crystal dimers: influence of chalcogen linkage and mesogenic-arm symmetry on the incidence and stability of the twist-bend nematic phase, *Chem. – A Eur. J.* 26 (2020) 3767–3775, <https://doi.org/10.1002/chem.201905208>.
- [29] Y. Arakawa, K. Komatsu, H. Tsuji, Twist-bend nematic liquid crystals based on thioether linkage, *New J. Chem.* 43 (17) (2019) 6786–6793.
- [30] E. Cruickshank, M. Salamończyk, D. Pocięcha, G.J. Strachan, J.M.D. Storey, C. Wang, J. Feng, C. Zhu, E. Gorecka, C.T. Imrie, Sulfur-linked cyanobiphenyl-based liquid crystal dimers and the twist-bend nematic phase, *Liq. Cryst.* 46 (10) (2019) 1595–1609, <https://doi.org/10.1080/02678292.2019.1641638>.
- [31] H.-C. Lee, Z. Lu, P.A. Henderson, M.F. Achard, W.A.K. Mahmood, G.-Y. Yeap, C.T. Imrie, Cholesteryl-based liquid crystal dimers containing a sulfur–sulfur link in the flexible spacer, *Liq. Cryst.* 39 (2) (2012) 259–268, <https://doi.org/10.1080/02678292.2011.641753>.
- [32] R. Walker, D. Pocięcha, G.J. Strachan, J.M.D. Storey, E. Gorecka, C.T. Imrie, Molecular curvature, specific intermolecular interactions and the twist-bend nematic phase: the synthesis and characterisation of the 1-(4-cyanobiphenyl-4'-yl)-6-(4-alkylanilinebenzylidene-4'-oxy)hexanes (CB6O.m), *Soft Matter*. 15 (2019) 3188–3197, <https://doi.org/10.1039/c9sm00026g>.
- [33] D.A. Paterson, C.A. Crawford, D. Pocięcha, R. Walker, J.M.D. Storey, E. Gorecka, C.T. Imrie, The role of a terminal chain in promoting the twist-bend nematic phase: the synthesis and characterisation of the 1-(4-cyanobiphenyl-4'-yl)-6-(4-alkyloxylanilinebenzylidene-4'-oxy)hexanes, *Liq. Cryst.* 45 (2018) 2341–2351, <https://doi.org/10.1080/02678292.2018.1525503>.
- [34] N. Avci, V. Borshch, D.D. Sarkar, R. Deb, G. Venkatesh, T. Turiv, S.V. Shivanovskii, N.V.S. Rao, O.D. Lavrentovich, Viscoelasticity, dielectric anisotropy, and birefringence in the nematic phase of three four-ring bent-core liquid crystals with an L-shaped molecular frame, *Soft Matter*. 9 (4) (2013) 1066–1075.
- [35] S. Lee, H. Kim, E. Tsai, J.M. Richardson, E. Korblova, D.M. Walba, N.A. Clark, S.B. Lee, D.K. Yoon, Multidimensional helical nanostructures in multiscale nanochannels, *Langmuir*. 31 (29) (2015) 8156–8161, <https://doi.org/10.1021/acs.langmuir.5b01620>.
- [36] M. Ali, E. Gorecka, D. Pocięcha, N. Vaupotič, Structure and grating efficiency of thin cells filled by a twist-bend nematic liquid crystal, *Phys. Rev. E*. 102 (2020) 032704, <https://doi.org/10.1103/PhysRevE.102.032704>.
- [37] C. Meyer, G.R. Luckhurst, 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* 3 (2) (2015) 318–328.
- [38] D. Pocięcha, C. Crawford, D.A. Paterson, J.M.D. Storey, C.T. Imrie, N. Vaupotič, E. Gorecka, Nature of nematic to twist bend nematic phase transition, *Phys. Rev. E*. 98 (2018) 052706, <https://doi.org/10.1103/PhysRevE.98.052706>.
- [39] B.K. Sadashiva, R. Amaranatha Reddy, R. Pratibha, N.V. Madhusudana, Biaxial smectic A phase in homologous series of compounds composed of highly polar unsymmetrically substituted bent-core molecules, *J. Mater. Chem.* 12 (2002) 943–950, <https://doi.org/10.1039/b109546c>.
- [40] V. Padmini, P.N. Babu, G.G. Nair, D.S.S. Rao, C.V. Yelamaggad, Optically biaxial, re-entrant and frustrated mesophases in chiral, non-symmetric liquid crystal dimers and binary mixtures, *Chem. – Asian J.* 11 (2020) 2897–2910, <https://doi.org/10.1002/asia.201600918>.
- [41] D. Pocięcha, N. Vaupotič, M. Majewska, E. Cruickshank, R. Walker, J.M.D. Storey, C.T. Imrie, C. Wang, E. Gorecka, Photonic bandgap in achiral liquid crystals—a twist on a twist, *Adv. Mater.* (2021) 2103288, <https://doi.org/10.1002/adma.202103288>.
- [42] L.E. Hough, M. Spannuth, M. Nakata, D.A. Coleman, C.D. Jones, G. Dantlgraber, C. Tschierske, J. Watanabe, E. Korblova, D.M. Walba, J.E. MacLennan, M.A. Glaser, N.A. Clark, Chiral isotropic liquids from achiral molecules, *Science*. 325 (5939) (2009) 452–456.
- [43] J. Matraszek, N. Topnani, N. Vaupotič, H. Takezoe, J. Mieczkowski, D. Pocięcha, E. Gorecka, Monolayer filaments versus multilayer stacking of bent-core molecules, *Angew. Chemie Int. Ed.* 55 (10) (2016) 3468–3472, <https://doi.org/10.1002/anie.201510123>.
- [44] L. Foley, W. Park, M. Yang, E. Carlson, E. Korblova, D.K. Yoon, D.M. Walba, Nanocombination of the low-temperature dark conglomerate: structural control from focal conics to helical nanofilaments, *Chem. – A Eur. J.* 25 (2019) 7438–7442, <https://doi.org/10.1002/chem.201900653>.
- [45] E. Cruickshank, G.J. Strachan, J.M. Storey, C.T. Imrie, Chalcogen bonding and liquid crystallinity: Understanding the anomalous behaviour of the 4'-(alkylthio)[1,1'-biphenyl]-4-carbonitriles (nSCB), *J. Mol. Liq.* (2021) 117094, <https://doi.org/10.1016/j.molliq.2021.117094>.
- [46] A. Zep, K. Sitkowska, D. Pocięcha, E. Gorecka, Photoresponsive helical nanofilaments of B4 phase, *J. Mater. Chem. C* 2 (13) (2014) 2323–2327.
- [47] E. Tsai, J.M. Richardson, E. Korblova, M. Nakata, D. Chen, Y. Shen, R. Shao, N.A. Clark, D.M. Walba, A modulated helical nanofilament phase, *Angew. Chemie*. 52 (20) (2013) 5254–5257.