Enantiotropic Nematics From Cross-Like 1,2,4,5-Tetrakis(4'-Alkyl-4-Ethynylbiphenyl)Benzenes And Their Biaxiality Studies

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In memory of Lian-Jye Yu

Abstract: The theoretically predicted optimum length/breadth/width ratio for maximizing shape biaxiality was investigated experimentally by the facile and successful synthesis of crossshaped compound 3, which showed enantiomeric nematic phase behavior. This cross-like core structure could alternatively be viewed as two fused Vshaped mesogens, which have recently immerged as a new direction in biaxial nematic research, at the bending tips that can act as a new structure for biaxial investigations. Whilst the thermal analysis data of compound 3 did not meet the expected theoretical values for biaxial nematics, surface-induced biaxiality was evidenced by optical studies. Cluster-size analysis within the nematic phase of compound 3 revealed the formation of meta-cybotactic nematics, which approached the cluster sizes of cybotactic nematics. The split small-angle 2D X-ray diffraction patterns of magnetic-field-aligned samples

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indicated that the nematic phase was composed of small smectic C-like clusters with the tilting of molecules within the clusters. The wide-temperaturerange enantiomeric nematic phase of cross-like compound 3 enabled the molecular skeleton to serve as an alternative skeleton to bent-rod mesogens, which exhibited nematic phases with the potential competition of transitions higher-order liquid-crystalline to phases and crystallization, for future biaxial investigations.

Introduction

The theoretical prediction^[1] of biaxial nematics (N_b) was first proposed more than four decades ago and, since then, much effort has been devoted to the realization of this exotic phase from low-molecular-weight thermotropic liquid crystals, which have promising applications for improving the response times and viewing-angle characteristics of liquid-crystal displays.^[2,3] Two main approaches have been

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proposed to afford the N_b phase in thermotropic systems: 1) by mixing rod/disc mesogens physically or chemically^[4] or 2) by achieving the shape biaxiality of a single component.^[5-7] In terms of shape biaxiality, board-like nematogens were originally proposed to lead to the N_b phase; however, all board-like or cross-like mesogens reported to date have shown only monotropic nematic behavior or columnar phases. For example, Goodby and co-workers reported the synthesis of board-like, or, more precisely, cross-like (Figure 1 a). 1,2,4,5-tetrakis(4-tridecylphenylethynyl)benzene (1), which showed a monotropic nematic phase within a small temperature range and its poor liquid crystallinity, which was ascribed to its structural deviation from being rod-like and disc-like, hindered further investigation of the nematic phase.^[5] Increasing the inter-core stacking interactions of board-like mesogens led to the disappearance of the nematic structure.^[6] The incorporation of molecular biaxiality into board-like Pd complexes generated a monotropic nematic phase with a weakly first-order nematic-to-isotropic (N-to-Iso) transition but a N_b phase could not be confirmed.^[7] The generation of biaxiality in thermotropic nematic LC systems by using the most-obvious model of boardlike molecules has yet to be successfully performed.

Recently, bent-core mesogens have immerged as a new direction in biaxial nematic research.^[8,9] Of the reported bentcore nematogens, Lehmann and co-workers reported

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Figure 1. a) Chemical structure of compound 1; b) schematic representation of the cross-like geometry, which can also be viewed as two bentcores that are fused at the bending tips; c) chemical structures of compounds 2 and 3.

a system with an ideal tetrahedral bending structure that fit the requirements to form a biaxial nematic phase.^[8] However, the nematic phases of bent-core mesogens typically have potential competition in the form of transitions into higherorder LC phases and crystallization.^[10] Nevertheless, the success in biaxial bent-core mesogens makes cross-like materials a good model for producing biaxiality because a cross can alternatively be viewed as two V-shaped mesogens that are fused at the bending tips (Figure 1b) to give a moresymmetrical molecular structure for wider LC ranges. However, as mentioned above, obtaining a reasonable nematic temperature range for cross-like molecules has been a major obstacle to further investigations of biaxiality. Better molecular design of lozenge-shaped mesogens is needed for the generation of wide-temperature-range nematic arrangements. Recently, with the aim of solving this problem, rigid Y-shaped nematogens that were derived from compound 1 were investigated to give stable nematic phases by the manipulation of intermolecular interaction through employing various substitution patterns on the central aromatic ring.^[11]



These results suggested that judicious molecular design for fine-tuning inter-cross-interactions for the generation of nematic supra-structures seems to be feasible to allow the exploration of their potential optical biaxiality. Herein, compounds 2 and 3 (Figure 1 c) were designed by extending the peripheral phenyl groups in cross-like compound 1 to biphenyl groups to retain the aspect ratio of 1.67 and to enhance inter-cross- π - π interactions between the side-arms. Enantiotropic nematic behavior over wide temperature ranges was achieved by the successful synthesis of cross-like compounds 3a-3d with biphenyl peripheries. A new platform for biaxial investigations is reported and investigations into the potential biaxiality of the nematic phase of compound 3d were conducted by using various methods, including conoscopy and 2D X-ray diffraction.

Results and Discussion

First, cross-like alkoxy derivative 2 was prepared because of its facile synthetic preparation (Scheme 1). However, difficulties in purification were encountered owing to the poor solubility of compound 2 in organic solvents and satisfactory elemental analysis was never achieved. Nevertheless, from preliminary differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) studies, compound 2 showed an enantiotropic nematic mesophase. Encouraged by these results, the synthesis of alkyl analogues (3) was carried out in the hope of solving the problem of low solubility for further investigations (Scheme 1). After various attempts, optimized yields of cross-like 1,2,4,5-tetrakis(4'alkyl-biphenyl-4-ethynyl)benzenes (3a-3d) of 73-95% were achieved by reacting 10 equivalents of the biphenyl-containing side-arm with 1,2,4,5-tetrabromobenzene under the coupling conditions described in the Experimental Section. Starting from tetraiodobenzene instead of its bromo analogue did not give higher yields. Compounds 3 are soluble in



Scheme 1. Synthesis of compounds 2 and 3.

most polar organic solvents, such as CH_2Cl_2 and THF. The facile and efficient synthesis of compounds **3** facilitated further investigations into the optical biaxiality of the mesophases.

The molecular structure of compound 3a was determined by single-crystal X-ray diffraction (Figure 2a). The molecular core of compound 3a is a rigid rectangular scaffold with an average length and width of 23.4 and 8.5 Å, respectively. The alkyl chains are approximately oriented along the long side of the core to furnish a prolonged molecular rectangle. Along the long molecular axis, chain interdigitations from adjacent molecules lead to the formation of an infinite 1Dchain structure (Figure 2b). Along the short axis, intermolecular π - π interactions are responsible for the sheet assembly. The π - π interactions are likely to be quadrupolar and, thus, should lead to a slipped-parallel arrangement of the molecules, as in the case of compound 3a, or an arrangement in which the minor axes are orthogonal. These sheets pile to render the overall molecular packing with parallel molecular planes, long axes, and short axes, respectively (Figure 2 c).

It has been proposed by using molecular field theory that



Figure 2. Single-crystal X-ray diffraction studies: a) the molecular structure of compound **3a** and packing diagrams normal to (b) and parallel to the molecular plane (c).

the maximum shape biaxiality can be reached when the biaxiality parameter (λ) is equal to 6^{-1/2}, which implies a specific length/breath/width (LBW) ratio of effectively 15:5:3.^[12] From the single-crystal structure, the biaxiality parameter and LBW ratio of the core of compound **3a**, assuming that the thickness of the molecule is 4.5 Å,^[10] were determined to be 0.50273 and about 15:5:4:2.9, respectively, which were close to their respective optimum values.

The mesogenic properties of compounds 3a-3d, which were studied by a combination of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), are summarized in Table 1. Upon heating, Schlieren or marbled textures, which are indicative of a nematic mesophase,

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Table 1. Phase behavior of compounds **3a-3d**.^[a]

Compound	Phase behavior	$T [^{\circ}C] (\Delta H [kJ mol^{-1}])$	$\Delta S/R$
3a	$Cryst \rightarrow N \rightarrow Iso_{p.d.}$	236.0 (50.74), 250.6 (0.74 ^[b])	_[c]
3b	$Cryst \rightarrow N \rightarrow Iso_{p.d.}$	192.3 (45.50), 232.3 (0.73)	_[c]
3 c	$Cryst \rightarrow N \rightarrow Iso_{p.d.}$	162.1 (36.54), 197.9 (0.88)	0.22
3 d	$Cryst \!\rightarrow\! N \!\rightarrow\! Iso$	149.9 (45.24), 190.9 (1.20)	0.31

[a] Cryst, N, Iso, and Iso_{p.d.} denote crystalline, nematic, and isotropic phases, and an isotropic liquid with partial decomposition, respectively. For compounds **3a–3c**, owing to thermal decomposition upon clearing, the data were obtained from the first DSC heating run at 10°Cmin⁻¹. For compound **3d**, the data were obtained from the second DSC heating run at 10°Cmin⁻¹. [b] The transition was accompanied by a severe thermal decomposition. [c] The N \rightarrow Iso transition was accompanied by severe decomposition and the $\Delta S/R$ value could not be unambiguously determined.

followed by dark homeotropic textures prior to clearing, were observed for all compounds. When approaching isotropic temperatures, compounds 3c and 3d showed flickering dark/bright textures. The Schlieren textures of the nematic phase of compounds 3a-3d that were sandwiched between glass slides showed solely two-brush disclinations (Figure 3a,b) upon slow cooling or slow heating (\pm



Figure 3. Optical micrographs of a) compound **3c** (heating 183 °C) and b) compound **3d** (cooling 160 °C), sandwiched between glass slides between cross-polarizers. Scale bar: 50 µm.

1°Cmin⁻¹). With increasing chain length, both the melting and clearing temperatures decreased whilst a general trend in increasing the mesophase range was observed, although the mesophase ranges of compounds 3a and 3b could not be unambiguously determined owing to severe thermal decomposition prior to clearing. The nematic temperature range of compound **3a** is 15° and those for compounds **3b**, 3c, and 3d are 40° or more. Compound 3d is the only compound that did not suffer from thermal decomposition prior to clearing and an enantiotropic nematic phase could be obtained. The enantiotropic behavior of the nematic phase of compound 3, contrary to the monotropic nematic behavior of compound 1, can be attributed to the incorporation of biphenyl groups for increasing intermolecular π - π interactions, presumably electrostatic quadrupolar interactions to lead to a slipped-parallel arrangement, similar to the packing pattern that is observed in the crystal structure. Moreover, the larger L/W and B/W ratios of compounds 3 than those of compound 1 give rise to more-restricted rotations along the long and short molecular axes to give enhanced intermolecular π - π interactions.



It has been predicted by theory that the optimal bending angle of the bent rods for maximum biaxiality is 109.5°.[13] When viewing compound 3 as two bent rods that are fused at the bending tips, the two types of interarm bending angles are approximately 60° and 120°, which are significantly off from the optimal value. The theory predicts that such a system should show a uniaxial nematic (N_{u}) phase with a biaxial nematic phase, which will not be detected by DSC, hidden below the freezing point. According to this theory, the biaxial nematic phases of compounds 3c and **3d** would not be observable. For compounds 3c and 3d, no transition was detected between the Cryst \rightarrow N and N \rightarrow Iso transitions by POM and DSC. It was also predicted by theory that the $N_{\rm b} \rightarrow$ Iso transition should be second order^[3,14] and that the entropy change $(\Delta S/R)$ should approach zero (when



Figure 4. Conoscopic interference figures with a) a λ -plate inserted and b) a l/4 plate inserted for the nematic phases of compounds **4** (66 °C), **3d** (176 °C), and **5** (80 °C) for the determination of the optical sign and optical biaxiality of the nematic phase of compound **3d**, respectively. The arrow denotes the rubbing direction.

 λ is the ideal value of $6^{-1/2}$) or be significantly smaller (when λ is away from the ideal value) than those for the N_u \rightarrow Iso transitions (≥ 0.4). For compounds **3c** and **3d**, which have minimal thermal decomposition, the $\Delta S/R$ values were 0.22 and 0.31, respectively; these values are not much smaller than 0.4 and, thus, suggest that the nematic phases are not biaxial. These values may have reflected the λ value of compounds **3** from the crystal structure, which was off the ideal value.

The molecular biaxiality of cross-like compounds 3 and the calamitic nature of the resulting nematic structure were confirmed by single-crystal structure determination, whereby the biaxial nematic molecular packing would rely on the restricted rotation along the long and short molecular axes, which may be understood by determination of the optical sign. By conoscopic studies on the homeotropically aligned sample with the insertion of a lambda retardation plate, the optical sign of the nematic phases of cross-like compound 3d, calamitic compound 4,^[15] and discotic compound 5^[16] were investigated and compared. Discotic compound 5 was chosen for the conoscopic studies because it was the only discotic compound that showed homeotropic alignment by the alignment method in this study. As shown in Figure 4a, for the optically positive nematic phase of compound 4, an interference pattern of yellow vertices of the second/fourth quadrants (quadrants of addition) and blue vertices of the first/third quadrants (quadrants of subtraction) was observed. For the optically negative uniaxial nematic phase of compound 5c, oppositely placed colors of the vertices of the quadrants were observed. The homeotropic alignment of the nematic phase of compound 3d, which was achieved by sandwiching the sample between rubbed poly(vinylalcohol) (PVA)-coated glass slides that were separated by a spacer of 5 µm thickness, was confirmed by its indistinguishable dark texture with the dark image of a blank cell under the same POM conditions (see the Supporting Information, Figure S1). No birefringence was observed for the homeotropic texture of compound 3d, which may imply that its nematic phase is non-biaxial or that it consists of small biaxial nematic domains that are isotropically distributed. For cross-like compound **3d**, the colors of the vertices resemble those of optically negative discotic compound 5, although not as distinct (Figure 4b), thus suggesting that the large index of refraction is parallel to the plane of the substrate.

For the nematic phase of compound **3d**, its calamitic nature implies that the chains are orientated along the long axis of the molecular core and the negative optical sign may imply that the rotations of the core along the long and short molecular axes are limited. These results imply that the nematic phase is a biaxial nematic phase.

Conoscopy was further utilized for the realization of optical axiality of the nematic phase of compound **3d**. Prior to the conoscopic studies, the homeotropic alignment of the nematic phase of compound **3d** was again confirmed. As shown in Figure 4b, the interference pattern of the hyperbolic figures, that is, the open isogyres, of the homeotropi-

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cally aligned nematic phase of compound **3d** corroborates its optical biaxiality, as opposed to those of cross-isogyres for calamitic compound $4^{[15]}$ and discotic compound $5^{[16]}$ both of which are uniaxial.

The mesophases of compounds **3** were further elaborated by X-ray diffraction (XRD) analysis (Table 2). As an example, the 2D XRD pattern of the crystalline state of compound **3d** revealed multiple rings with sharp intensities (Figure 5a). When entering the mesophase, only two rings were observed. The broader halo in the wide-angle regime (*d*spacing ≈ 4.8 Å) corresponds to the correlation of the molten alkyl chains, thereby confirming the formation of the

mesophase. The wide-angle signal may also include the inter-disc correlation along the disc-normal but this fact could not be verified. The sharper signal in the small-angle region corresponds to inter-core correlations along the long molecular axis. With increasing chain length, the *d*-spacing of the small-angle signals increases.

Under an applied magnetic field (B) of 0.3 T normal to the X-ray beam and capillary, the two rings of the nematic phase of compound 3d were no longer circular and were centered orthogonally to each other. In the wide-angle regime, a pair of alkyl halos appeared (Figure 5b), the intensities of which peaked on the equator (perpendicular to B). In the small-angle region, two pairs of sharp arcs were detected along the meridian (Figure 5c). As shown in the azimuthal scan over $2\theta = 2-4^{\circ}$ (Figure 5d), the splitting angles $(\Delta \chi/2)$ were (43-44°, nearly identical Table 3) within the nematic temperatures and the splitting becomes less distinct as the temperature approaches the clearing point. On further heating to the isotropic phase, the pair of split arcs collapses into two arcs with the maximum intensities along meridian. Compound 3c also exhibited split small-angle scattering in the nematic temperature range with splitting angles $(\Delta \gamma/2)$ of 44° (Table 3; also see the Supporting Information, Figure S4).

It has been reported that the small-angle-signal splitting of magnetically aligned nematics could originate from a tilted organization in *meta*-cybotactic nematic phases, which are composed of locally ordered smectic C (SmC)

Table 2. Powder X-ray diffraction data of compounds 3a-3d.

Compound	<i>T</i> [°C]	d-Spacing [Å]		
3a	245	24.3, 4.9		
3b	225	26.2, 4.9		
3c	190	29.1, 4.8		
3 d	185	33.6, 4.8		



Figure 5. Variable-temperature 2D XRD patterns of compound **3d**: a) unaligned; b) aligned by a 0.3 T magnetic field; c) zoomed-in plots of the small-angle regions in (b); d) azimuthal scans of $2\theta = 2-4^{\circ}$ of (c) at 165, 175, 185, and 190 °C.

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Table 3. Variable-temperature cluster size $(L_{||} \text{ and } L_{\&\#8869:})$ and splitting $(\Delta \chi/2)$ of the small-angle XRD scattering in the nematic phase of magnetically aligned samples of compounds **3c** and **3d**.

Compound	В	T ^[a]	$d^{[b]}$	Δχ	$\Delta \chi/2$	L_{11}	L_{\perp}
	[T]	[°C]	[Å]	[°]	[°]	[Å]	[Å]
3d	0.3	165	35.3	85	43	62	8
		175	34.7	85	43	62	7
		185	34.0	87	44	61	7
	0	175	33.8	_	-	64	10
		185	33.6	_	-	64	10
3c	0.3	170	31.7	87	44	40	7
		180	31.6	88	44	44	8
		190	29.9	87	44	35	8
	0	180	29.2	_	-	42	10
		185	29.1	-	-	42	10

[a] Temperature on heating. [b] d-Spacing of the small-angle scattering.

clusters, and/or the biaxial cybotactic nematic phase.^[10,17-20] Herein, the term "meta-cybotactic phase" represents the nematic phase of clusters that, in some literature reports, are called cybotactic nematics and the term "cybotactic phase" represents the normal nematic phase with very short-range, non-specific, nearest-neighbor molecular packing, which, in some literature reports, is called classical cybotactic or ordinary nematics.^[10,17-20] Simulations have shown that the form factor, that is, molecular structure, dominates in biaxial cybotactic nematics, to exhibit temperature-independent splitting, whilst the structure factor, that is, the correlation of molecular packing, dictates in meta-cybotactic nematics, to give temperature-dependent splitting.^[21] Moreover, the splitting that is caused by the form factor will be considerably larger than that caused by the structure factor.^[21] The temperature-independent splitting by the form factor can be easily understood because rigid core structures do not significantly distort as the temperature changes. On the other hand, tilting of the smectic-like clusters in meta-cybotactic nematics may change upon variation in the temperature. Experimentally, for bent-rod mesogens, $\Delta \chi/2$ increased with increasing temperature within meta-cybotactic nematics, whereas $\Delta \chi/2$ decreased within cybotactic nematics.^[19] Moreover, for bent-rods nematics, the $\Delta \chi/2$ values increase with shortening chain length in the meta-cybotactic arrangement and stay roughly constant with changing the chain length in cybotactic nematics.^[10,19] For both compounds 3c and 3d, the differences in the $\Delta \chi/2$ values in the their nematic phase at different temperatures are within 1° (Table 3). However, the temperature dependence was only investigated only over 20 K, whereas the trends in previous reports were observed over much-wider temperature ranges.^[10,19] Moreover, the difference in chain length between compounds 3c and 3d is only two carbon atoms. Therefore, the chain-length- and temperature dependence of $\Delta \chi/2$ of compounds **3c** and **3d** may have not been truly revealed by the data within the 20 K range that was investigated.

The strong applied field that was used herein may induce the formation of the *meta*-cybotactic nematic arrangement and the relatively higher-intensity of the small-angle signal



Figure 6. Variable-temperature 1D X-ray diffractograms of magneticfield-aligned compound **3d** (normalized to the same intensity of the wide-angle signal); Inset: a zoomed-in plot of the small-angle signals.

with respect to that of the wide-angle signal of compound 3 (Figure 6) raises the question of a field-induced meta-cybotactic nematic arrangement.^[18] It has been reported that, for nematic phases, a much-stronger small-angle-scattering intensity than the wide-angle-scattering intensity would suggest a meta-cybotactic nematic phase.^[20] In the XRD pattern of the nematic phase of compound 3d at various temperatures (Figure 6), the small-angle-scattering intensity is much stronger than the wide-angle-scattering intensity. Quantitatively, meta-cybotactics can be distinguished by their significantly larger cluster sizes, that is, considerably larger correlation lengths with $L_{\parallel}/d_{\parallel} \ge 2$ and $L_{\perp}/d_{\perp} \approx 10$ than those of cybotactics, which only have nearest-neighbor correlation with $L_{\parallel}/d_{\parallel} \approx 2$ and $L_{\perp}/d_{\perp} \approx 4$.^[20] For compound **3d**, without the applied magnetic field, the longitudinal and transverse cluster sizes $(L_{||}$ and L_{\perp} , respectively) by using Scherrer's equation^[22] within the nematic temperature range at 165 and 175 °C are about 55 (d=34.5 Å) and 9 Å (d=4.8 Å), respectively, without the applied magnetic field and about 62 Å (d=35.0 Å) and 8 Å (d=4.8 Å), respectively, under the applied field (Table 3). For compound 3d, the applied magnetic field results in a small change in both L_{\perp} and L_{\perp} : a small increase in L_{\perp} , and a small decrease in L_{\perp} . The longitudinal and transversal L/d values are both approximately 2, thus suggesting that the nematic phase of compound 3d is (classical) cybotactic. Notably, cluster sizes that are determined by using the Scherrer equation are only estimations and that, when cluster sizes are translated into their corresponding numbers of molecules (L/d+1), the difference will be less significant. The respective cluster sizes of $L_{||}$ and L_{\perp} in the nematic phase of compound 3d correspond to an aggregate of about three molecules in both the longitudinal and transversal directions, that is, a short-range small cluster of $3 \times 3 \times$ 3 molecules. The almost-field-independent cluster sizes indicate that the magnetic field did not induce further clustering of compound 3d. In summary, the cluster-size calculation suggests that the clusters in the nematic phase of compound 3d are small, which suggests a classical cybotactic nematic.



Similar results were found for compound **3c**, but with smaller cluster sizes (Table 3).

For cross-like molecules of compounds 3, three distinct scatterings, owing to the length, width, and breadth correlations, could most probably be indicative of a biaxial arrangement. For the biaxial packing of cross-like compounds 3, the scattering that is due to the length correlation is apparent and those that are due to the other two dimensions are not apparent. For compounds 3, the minimum achievable average thickness, that is, breadth, of compounds 3, by allowing the rotational disorder of the biphenyl groups along the respective sidearm axis, is about 4.5 Å,^[10] which is very close to the *d*-spacing of the alkyl halo. Because the wide-angle scattering is very diffuse in the nematic phases, the differentiation of signals owing to molecular width and breadth from the alkyl halo is not apparent for the nematic phase of compound 3. However, when comparing the 1D diffractograms of compound 3d in the nematic phase with that in the isotropic phase (Figure 6), two very broad signals at 10.2 (2θ $\approx 10.2^{\circ}$) and 3.2 Å ($2\theta \approx 23.9^{\circ}$) can be observed that may be attributed to the molecular width and breadth correlations, respectively. The cross-like molecules in the nematic phase are likely to be weakly associated to render the observed weak and broad correlation along the width dimension. More likely, the molecules can pack in a slipped-parallel manner in the clusters, similar to the pattern that is observed in the crystal structure, rather than in a side-by-side manner, to show split small-angle scattering in the aligned samples. Under a magnetic field, the nematic phase of compounds 3c and 3d are composed of aligned small clusters, that is, short-range molecular organization of about three molecules, both along the long/short molecular axis and perpendicular to the molecular plane. Within each small cluster, the molecules pack in an in-plane, slipped-parallel organization along the molecular plane, thereby resembling the SmC-like organization. Such organization will lead to split small-angle scattering, as observed in Figure 5c.

Figure 7 shows the XRD setup and the proposed molecular packing of short-range SmC-like clusters in the nematic phase of compounds 3 based on the 2D XRD results. Two possible SmC-like cluster orientations are proposed (for detailed analysis of 2D XRD and molecular packing, see the Supporting Information, Figures S7, S8, and S9). Figure 7b demonstrates the SmC-like cluster packing when the long molecular axis is aligned along the magnetic field. Two alternative views of the structure of compound 3, as two tilted rods that are fused at the center of the rods (Figure 7b, left panel) or as two V-shaped mesogens that are fused at the bending tips (Figure 7b: right panel), both render the same 2D XRD patterns (Figure 5c). In Figure 7c, the SmC-like clusters are orientated so that one of the long rods in the cross that is formed by fusing two tilted rods at the centers is aligned along the magnetic field. Herein, the two types of clusters with opposite tilting directions with respect to the magnetic field are both present to lead to the obtained XRD pattern.



Figure 7. a) XRD experimental setup, in which the sample is shown as a three-cluster aggregate and b,c) the proposed molecular packing in a *SmC*-like cluster. (b) A *SmC*-like cluster, which shows two alternative views of the structure of compound **3** as two tilted rods that are fused at the centers of the rods (left) or as two V-shaped mesogens that are fused at the bending tips (right). Herein, the long molecular axis is aligned along the magnetic field (*B*). (c) *SmC*-like clusters with compound **3**; the samples are viewed as two fused cross-rods and one of the long rods is aligned along the magnetic field. In (b) and (c), short dashed lines represent the layer planes.

Conclusion

The theoretically predicted optimum length/breadth/width ratio for maximizing shape biaxiality was investigated experimentally by the successful synthesis of compound **3**. The wide temperature range of the nematic phase that was exhibited by compound **3** enabled further biaxiality studies. The thermal analysis data, $\Delta S/R$, did not meet the expected theoretical values for biaxial nematics. The conoscopy studies indicated the presence of restricted rotations along the long- and short molecular axes within the molecular packing. Cluster-size analysis within the nematic phase of com-

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pounds 3c and 3d indicated that their nematic phase was N_{cvbC} and the split small-angle 2D XRD patterns of magnetic-field-aligned samples suggested an approximate 44° tilting of the molecules within the clusters. Moreover, the enantiotropic nematic behavior of cross-like compound 3 was observed without the detection of other higher-order mesophases; this result is in contrast to the nematic phases of bent-core mesogens, which face potential competition from transitions into higher-order LC phases and crystallization. Contrary to numerous previously reported attempts to generate enantiotropic nematics from board-like- and cross-like molecules, the results reported herein should evoke a renaissance in interest in the investigation of biaxiality on boardlike or cross-like nematogens. The wide-temperature-range nematic phases of compound 3 enable the molecular skeleton to act as an alternative skeleton to bent-rod nematogens for future biaxial investigations. Further structural modification to afford lower melting points, expanding the nematic temperature range, and to induce biaxiality, for example by the incorporation of molecular biaxiality,^[7] will be pursued in the near future.

Experimental Section

All reactions were conducted under an atmosphere of nitrogen in ovendried glassware by using standard Schlenk techniques. THF was distilled over sodium/benzophenone. All other solvents and chemicals were reagent grade (Aldrich Chemical Co.) and used without further purification unless otherwise described. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 600 spectrometer. Chemical shifts are reported in ppm relative to residual CHCl₃ (¹H: $\delta = 7.26$ ppm; ¹³C: $\delta = 77.0$ ppm). Absorption spectra were recorded on a Jasco V-550 spectrometer. Photoluminescence spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was measured on a PerkinElmer Pyris1 with heating and cooling rates of 5 and 10°C min⁻¹, respectively. Polarized optical microscopy (POM) was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. Conoscopic studies were performed by sandwiching samples between two rubbed glass slides that were separated by a $5\,\mu m$ spacer. Powder X-ray diffraction data were collected on the wiggler beam-line BL17A at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, by using a triangular bent Si(111) monochromator and a wavelength of 1.333621 Å. The sample was packed into a 1 mm capillary and mounted on the Huber 5020 diffractometer. A heat gun was equipped at the BL17A beamline and the temperature controller was programmable by a PC with a PID feedback system. The 2D XRD patterns were obtained on samples that were aligned by one SmCo permanent magnet pair. Mass spectra were obtained on a Jeol JMS-700 Mstation at the NSC Regional Instrumental Center at National Central University (Chungli, Taiwan) and elemental analysis was carried out on a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Cheng Kung University (Tainan, Taiwan). X-ray structural characterization of compound 3a was carried out on a Bruker Nonius Kappa CCD diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by using direct methods and refined with SHELXL-97.^[23] All of the non-hydrogen atoms were refined with anisotropic temperature factors.

CCDC-887798 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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 - $\lambda = (3/2)^{1/2} L(B-W) / [L(B+W) 2BW]$ (1) $\lambda = 6^{-1/2} \approx 0.40825 \text{ when } B^{-1} = (W^{-1}L^{-1})/2$ (2)
 - $\lambda = 6^{-1/2} \approx 0.40825$ when $B^{-1} = (W^{-1}L^{-1})/2$ (2) However, the LBW ratio of 5:3:1 in Equation (1) gives $\lambda = 0.87482$.
 - The best LBW ratio (15:5:3) is calculated herein.
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Enantiotropic Nematics From Cross-Like 1,2,4,5-Tetrakis(4'-Alkyl-4-Ethynylbiphenyl)Benzenes And Their Biaxiality Studies



Take up your cross: An enantiotropic nematic phase with a wide temperature range has been achieved by using cross-like mesogens. Biaxiality investigations by using conoscopic and 2D XRD studies imply the formation of small smectic C-like *meta*-cybotactic clusters in the nematic arrangement.

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