Mesophases of Achiral Bent Molecules

F. C. Yu and L. J. Yu*

Department of Chemistry, Tamkang University, Tamsui, Taipei 25137, Taiwan

Received February 23, 2006. Revised Manuscript Received September 9, 2006

A systematic structural modification is carried out to change the molecular shapes of stilbene derivatives from rodlike through hockey stick then to bananalike by tuning the length of the functional group attached to the lateral direction of the rodlike skeletons. The mesophases and the corresponding properties are monitored by optical polarizing microscopy, differential scanning calorimetry, electric field effect, and X-ray diffraction. The existence of mesophase is strongly affected by the molecular conformation and intermolecular forces inherited in the moiety employed. Nematic, smectic C (SmC), and anticlinic smectic C (SmCa) phases are formed by the hockey stick molecules. Defects of 2- and 4-brushes are observed for the SmC and SmCa phases and indicate the existence of anticlinic arrangements of neighboring layers. Anticlinic layer structures constitute the intermediate phases between the calamitic and banana mesophases. Electric-field-switched texture changes are evident for the nematic and SmC phases and are different from those of known calamitic mesogens. These behaviors are ascribed to the bent conformation of these hockey stick molecules. Antiferroelectric B_2 banana phases are formed by hockey stick molecules with two arms carrying moieties of large enough polarizability.

Introduction

Banana mesophases formed by bent core (banana) mesogens have been a subfield of liquid crystal research recently because of great interest in academic research and their potential applications. Among the banana mesophases, the B_2 phases have attracted most of the attention because of their ferro- and antiferroelectric switching behaviors reported first by Niori et al.[1] and Link et al.[2] The structure of banana-phase-forming bent molecules consists of, in general, a bent unit connected with two aromatic arms that each end with a hydrocarbon chain; it is considered to be an achiral molecule.[1,3−5] Unlike the calamitic ferro- and antiferroelectric smectic phases, where a chiral moiety is required[6,7] for the constituting molecules, a chiral moiety is not required for the molecules to exhibit B_2 phases with electric-field-switchable properties. It is the correlation of the bent conformation and the tilt of the molecular director that results in the corresponding layered phases being electric-field active.[2] For the formation of banana phases, the equivalence of the arms of the bent molecule is not a requirement, because there have been reports of electric-field-switchable smectic phases (banana phases) comprised of achiral bent-core molecules with two arms having different numbers of phenyl rings.[8,9] It was reported that a polarization behavior was observed for a free-standing film of an anticlinic smectic C phase (SmCa) formed by hockey-stick-shaped molecules—a bent molecule with one of the arms consisting of only an aliphatic chain.[10] There were reports of peculiar smectic phases formed by bent molecules exhibiting unusual optical-switching behaviors.[11] These observations indicate that the bend conformation plays an interesting role in the mesophases exhibition of these important electric-field activities.

Considering the shapes of banana and hockey stick molecules, the banana molecules consist of two arms roughly equal and the hockey stick molecules two arms greatly different in length. These two types of molecules can be regarded as the resulting molecules from bending a long

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* Corresponding author. E-mail: ljyu@mail.tku.edu.tw.

(1) Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, J.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231.

(2) (a) Link, D. R.; Natale, G.; Shao, R.; Maclennan, J. E.; Clark, N. A.; Körblova, E.; Walba, D. M. *Science* **1997**, *278*, 1924. (b) Walba, D. M.; Körblova, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. *Science* **2000**, *288*, 2181−2184.

(3) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707.

(4) (a) Weissflog, W.; Lischka, C.; Benné, I.; Scharf, T.; Pelzl, G.; Diele, S.; Kruth, H. *Proc. SPIE−Int. Soc. Opt. Eng.* **1998**, *14*, 3319. (b) Diele, S.; Grande, S.; Kruth, H.; Lischka, C.; Pelzl, G.; Weissflog, W.; Wirth, I. *Ferroelectrics* **1998**, *212*, 169. (c) Pelzl, G.; Diele, S.; Jakli, A.; Lischka, C.; Wirth, I.; Weissflog, W. *Liq. Cryst.* **1999**, *26*, 135.

(5) (a) Amaranatha Reddy, R.; Raghunathan, V. A.; Sadashiva, B. K. *Chem. Mater.* **2005**, *17*, 274−283. (b) Amaranatha Reddy, R.; Sadashiva, B. K.; Raghunathan, V. A. *Chem. Mater.* **2004**, *16*, 4050−4062.

(6) Meyer, R. B.; Liébert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett. (Paris)* **1975**, *36*, L69−71.

(7) Chandani, A. D. L.; Gorecka, E.; Ouchi, Y.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* **1989**, *28*, L1265.

(8) (a) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C. *J. Am. Chem. Soc.* **2000**, *122*, 1593. (b) Dantlgraber, G.; Shen, D.; Diele, S.; Tschierske, C. *Chem. Mater.* **2002**, *14*, 1149. (c) Schröder, M. W.; Diele, S.; Pelzl, G.; Dunemann, U.; Kresse, H.; Weissflog, W. *J. Mater. Chem.* **2003**, *13*, 1877−1882. (d) Dunemann, U.; Schröder, M. W.; Pelzl, G.; Diele, S.; Weissflog, W. *Liq. Cryst.* **2005**, *32*, 151−161.

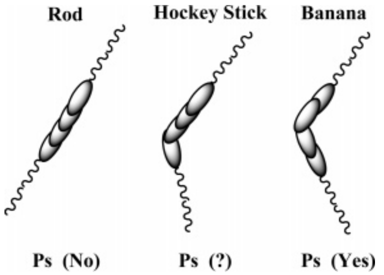
(9) (a) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *J. Mater. Chem.* **2005**, *15*, 2056−2064. (b) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *Liq. Cryst.* **2004**, *31*, 1347−1356. (c) Achten, R.; Cuypers, R.; Giesbers, M.; Koudijs, A.; Marcelis, A. T. M.; Sudhölter, E. J. R. *Liq. Cryst.* **2004**, *31*, 1167−1174.

(10) (a) Stannarius, R.; Li, J. J.; Weissflog, W. *Phys. Rev. Lett.* **2003**, *90*, 025502. (b) Das, B.; Grande, S.; Weissflog, W.; Eremin, A.; Schröder, M. W.; Pelzl, G.; Diele, S.; Kresse, H. *Liq. Cryst.* **2003**, *30*, 529.

(11) (a) Weissflog, W.; Dunemann, U.; Schröder, M. W.; Diele, S.; Pelzl, G.; Kresse, H.; Grande, S. *J. Mater. Chem.* **2005**, *15*, 939−946 and references therein. (b) Jakli, A.; Kruerke, D.; Sawade, H.; Heppke, G. *Phys. Rev. Lett.* **2001**, *86*, 5715−5718. (c) Lagerwall, J. P. P.; Giesselmann, F.; Wand, M. D.; Walba, D. W. *Chem. Mater.* **2004,** *16*, 3606−3615. (d) Cowling, S. J.; Hall, A. W.; Goodby, J, W. *Chem. Commun.* **2005**, 1546−1548.

10.1021/cm060459d CCC: $33.50

Scheme 1. Schematic Representations and Spontaneous Polarizations (Ps) of Achiral Rod, Hockey Stick, and Banana Molecules

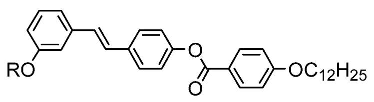


rodlike molecule symmetrically and unsymmetrically. When an achiral rodlike smectic C (SmC)-forming molecule is converted via structural modification through the hockey stick then to the banana shape, the corresponding mesophase is changed from nonferroelectric (achiral SmC) to ferro- or antiferroelectric (B_2 banana), Scheme 1. It is interesting then to inspect the roles played by this bending for the induction of spontaneous polarization of mesophases obtained during the structural modification. Structural variation can be achieved by tuning the length of the substituent attached to the lateral direction of a rodlike molecule. The mesophases and the corresponding physical properties of the derivatives thus obtained can be monitored closely. These results should shed some light regarding the occurrence of polarization in these mesophases and would be helpful for the understanding of the relationship between the polarization of the mesophase and molecular shape as well as for designing new mesogens in the future.

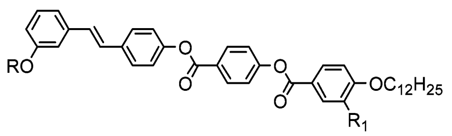
In the present study, the mesomorphism accompanying the variation of molecular shape from rodlike through hockey stick and then to bananalike was investigated. Rigid cores having three or four phenyl rings connected with a carbon−carbon double bond and ester linkages were used as the main skeletons, and substituents with various numbers of benzoate or cinnamate units were attached at the position meta to the double bond to vary the molecular shape. Meanwhile, dodecyloxy chains were used as the terminal chains at both ends. The mesophases of the derivatives obtained along the process of structural modification were examined by optical polarizing microscopy, differential scanning calorimetry, X-ray diffraction, and electric field effects. Molecular calculation was also carried out for the molecules studied here, considering that the results might be helpful in clarifying the relations of mesophase properties to the molecular conformation and the orientation of the dipole moment contained.

Experimental

The molecules studied were synthesized according to routes shown in Scheme 2. The starting compound, bromophenol, was reacted with 3,4-dihydro-2H-pyran (DHP) to yield the protected bromophenol (**A**).[12] The Heck reaction[13] was carried out for **A** and



3-ring skeleton



4-ring skeleton

4-acetoxystyrene and followed by deacetylation to yield the 4′-hydroxy- stilbene derivative **B**. Esterifications of this phenol derivative with 4-dodecyloxy benzoic acid or 4-(4-dodecyloxy benzoyloxy) benzoic acid were accomplished with 1,3-di-cyclohexyl carbodiimide (DCC) and 4-dimethylamino pyridine (DMAP)[14] to obtain THP-protected **2** and **3**, which were deprotected to yield compounds **2** and **3**. Products **2a** and **3a** were obtained after etherification of these phenols with 1-dodecanol in the presence of diethyl azodicarboxylate (DEAD) and triphenyl phosphine (Ph_3P).[15] Esterifications of **2** and **3** with various substituted benzoic acids, with the aid of DCC/DMAP, yielded the corresponding products **2b**−**e** and **3b**−**f**. The hydrogenation for the double bond of the stilbene (of **2e** and **3e**) was catalyzed by Pd/C in cyclohexene/ethanol solvent to obtain **2e′** and **3e′**.[16] The details of synthetic procedures and characterizations of the corresponding derivatives are included in the Supporting Information. The textures of the mesophases (temperature controller Mettler FP 80 and 82HT) were examined by optical polarizing microscopy (Nikon, OPITPHOT-POL); the phase transitions were studied by differential scanning calorimetry (Perkin-Elmer, Pyris 1); and the electric-field effects were studied by a DC field and the triangular-wave method. X-ray diffraction for the powder sample was conducted at the National Synchrotron Radiation Research Center (NSRRC, beam line 17A1), Taiwan.

Results

The phase behaviors, transition temperatures (from DSC), and enthalpy values of the corresponding phase transitions for the derivatives obtained from 3- and 4-ring skeletons, compounds **2s** and **3s**, are listed in Tables 1 and 2, respectively. It is noted that the phase-transition temperatures observed with optical polarizing microscopy are lower than those measured by DSC, particularly for thinner samples.

Dependence of the Mesophase on Structure Variation. Compound **1** (see Chart 1) exhibits typical calamitic mesophases, SmC and nematic, at relatively high temperatures, apparently due to the rather rigid core *p*-hydroxystilbene. With the hydroxyl group moved to the position meta to the double bond, compound **2**, the nematic phase is retained and the layered phase is diminished. As compared to **1**, both the melting and isotropisation temperatures are lowered, and more drastically for the latter. These drastic changes in physical properties can be attributed to the change in molecular shape, because all the constituting moieties are the same. Attachment of a long tail (a dodecyloxy chain) to

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(12) Kocienski, P. J. *Protecting Groups*; Georg Thieme Verlag Stuttgart: New York, 1994; 83.

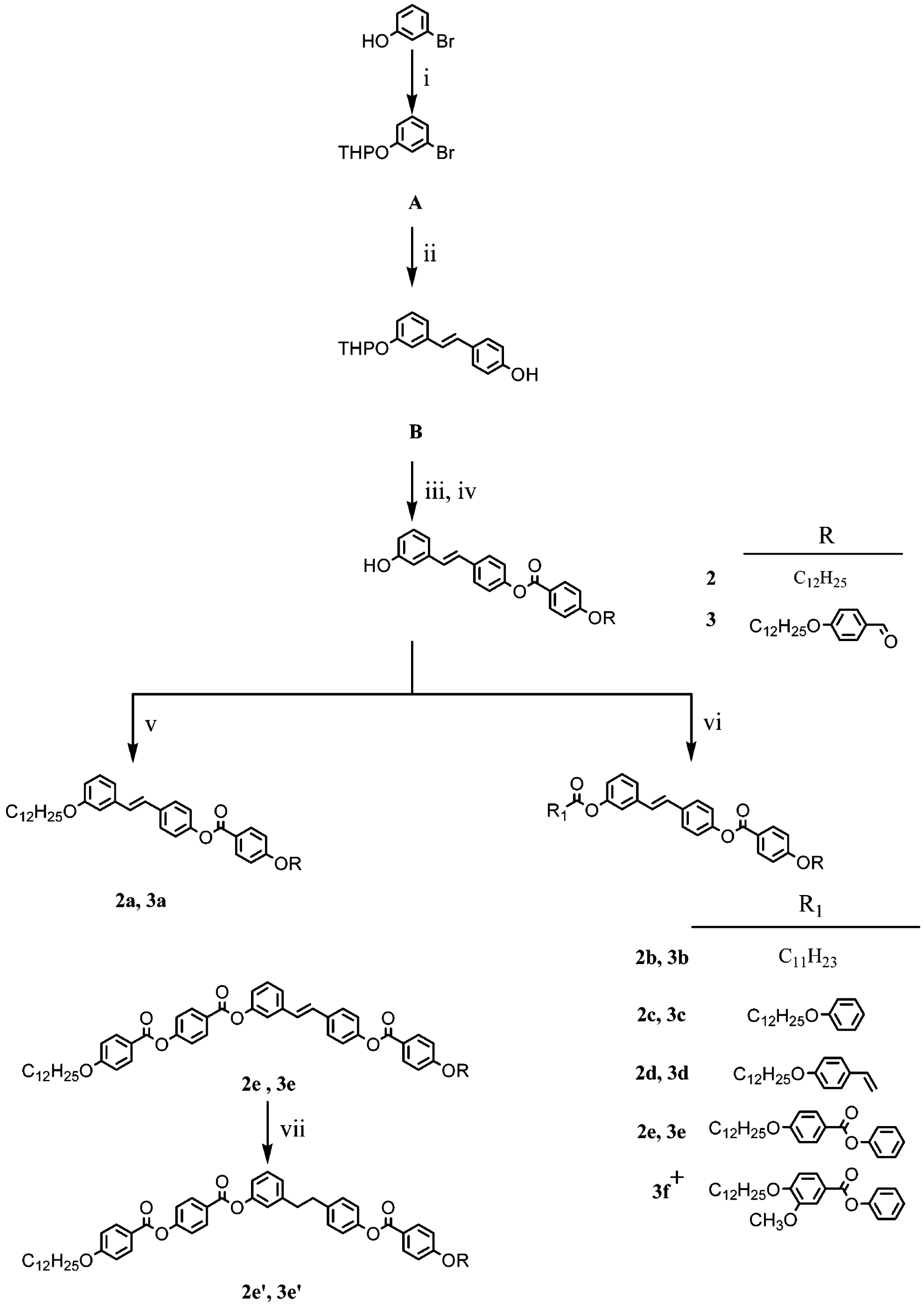
(13) (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (c) Heck, R. F. *Org. React.* **1982**, *27*, 345.

(14) Kocienski, P. J. *Protecting Groups*; Georg Thieme Verlag Stuttgart: New York, 1994; 120.

(15) Mitsunobu, O. *Synthesis* **1981**, 1.

(16) Hanessian, S.; Liak, T. J.; Vanasse, B. *Synthesis* **1981**, 396.

Scheme 2. Synthetic Routes for the Achiral Bent Molecules.

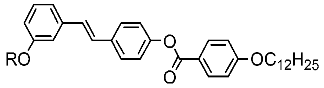


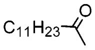
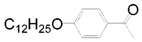
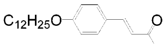
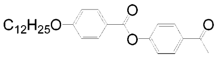
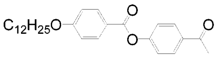
(i) Dihydropyran, PTSA, CH_2Cl_2, 30 min. (ii) (a) Acetoxystyrene, $Pd(OAc)_2$, $(o\text{-tol})_3P$, CH_3CN, Et_3N, 36 h; (b) KOH, THF, CH_3OH, 2 h. (iii) 4-Dodecyloxy benzoic acid (or 4-(4-dodecyloxybenzoyloxy) benzoic acid), DCC, DMAP, THF, 24 h. (iv) PTSA, THF, CH_3OH, 1 h. (v) 1-Dodecanol, DEAD, Ph_3P, CH_2Cl_2. (vi) R_1COOH, DCC, DMAP, THF. (vii) Pd−C, cyclohexene, EtOH. $^+$R is 3-methoxy-4-dodecyloxybenzoyl.

this meta position results in mesophases with layer structures restored (SmC and SmA) and nematic phase diminished (compound **2a**). This long-chain effect is similar to that frequently observed for calamitic mesogens, i.e., a long hydrocarbon chain promotes the formation of a layered phase. However, the corresponding phase temperatures are lowered further and accompanied with a narrowing of the mesophase temperature range. The lowering is more drastic for the isotropisation than the mp (melting point). These effects are apparently due to the bent molecular conformation.

Replacement of the ether linkage at the meta position of **2a** by an ester linkage resulted in compound **2b**, an elevation of the mp by 15 K, and no effect on the isotropisation temperature of the smectic phase. This result indicates that the bent conformation is maintained for **2b**, and the SmC phase becomes monotropic because of the elevation of mp. Insertion of an oxyphenyl unit (or an oxystyryl unit) along this lateral direction results in compounds **2c** (or **2d**) and a further slight increment of mp, but does not introduce any mesophase. A typical banana B_2 phase is observed after one more unit of benzoate is inserted (**2e**) that resembles a typical bent (banana) molecule but with nonequivalent arms. These results indicate that aromatic (or conjugated) moieties introduced along the lateral direction (**2c** and **2d**) certainly increase the interactions between the neighboring molecules, as have been reflected in the increments of mp. However, these interactions apparently are not strong enough to compensate the destroying effects on mesophase formation

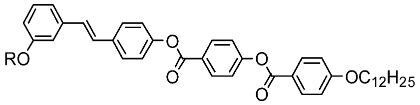
Table 1. Mesophases, Transition Temperature (°C), and Enthalpy Changes (kJ/mol) of the Corresponding Phase Transitions of 2s

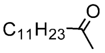
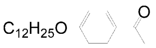
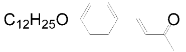
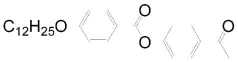
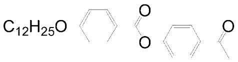
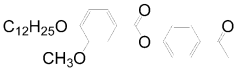


compound	R	Phase Sequences												
		K		B$_1$		B$_2$		SmC		SmA		N		I
2	H	•	129.9 [33.32]									•	158.9 [0.92]	•
2a	$C_{12}H_{25}$	•	77.2 [66.95]					•	80.1 [0.03]	•	80.3 [4.11]			•
2b		•	92.1 [69.10]					(•)^a	(80.2) [4.15]					•
2c		•	108.1 [45.75]											•
2d		•	111.5 [45.54]											•
2e		•	121.9 [25.02]			•	135.2 [21.69]							•
2e′^{b}		•	97.4 [56.04]			(•)^a	(94.4) [21.83]							•

^{a} Monotropic. ^{b} Diphenylethane instead of stilbene.

Table 2. Mesophases, Transition Temperature (°C), and Enthalpy Changes (kJ/mol) of the Corresponding Phase Transitions of 3s

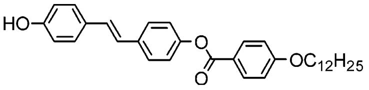


compound	R	Phase Sequences												
		K		B$_1$		B$_2$		SmCa		SmC		N		I
3a	$C_{12}H_{25}$	•	91.8 [52.01]					(•)^a	(86.6) [0.02]	•	161.4 [1.30]	•	165.7 [1.26]	•
3b		•	113.3 [43.69]							•	162.3 [2.41]	•	165.7 [1.11]	•
3c		•	133.6 [61.41]					(•)^a	(123.9) [1.59]			(•)^a	(125.1) [0.86]	•
3d		•	131.9 [57.56]	(•)^a	(118.3) [10.16]									•
3e		•	121.6 [44.07]			•	173.4 [21.50]							•
3e′^{b}		•	77.2 [66.95]	(•)^c										•
3f^d		•	86.3 [19.56]	•	105.9 [12.97]									•

^{a} Monotropic. ^{b} Diphenylethane instead of stilbene. ^{c} Observed by POM upon rapid cooling ^{d} Methoxy group at the 3-position of both terminal benzoate units.

because of the bent conformation and the bulkiness of these moieties. When the interaction forces are increased by incorporating appropriate moieties (**2e**) to overcome this destroying effect and hence raise the isotropisation temperature, a mesophase can exist. But the resulting molecular shape is no longer that of conventional calamitic mesogens and the organized phase structures are apparently different from that observed for the calamitic mesophases, although layered structures are maintained.

Chart 1



1

Cr 184.7[28.92] SmC 207.0[0.47] N 234.4[1.46] I

Considering the above observations, we then turned to molecules with a 4-ring skeleton. When one more benzoate unit was inserted in the main core, compound **3a**, both the mp and isotropisation temperatures were raised, 15 and 85 K, respectively, as compared to those of compound **2a**. The main consequences are the stabilization of SmC (with 70 K on heating) and nematic (4 K) phases. It is worth noting that a SmCa phase appears at 86.6 °C on cooling the SmC phase. Replacing the ether linkage by an ester linkage resulted in **3b** and a rise in mp by 21 K, a value slightly higher than that observed for changing **2a** to **2b**. The SmC and nematic mesophases remained unaffected. The SmCa phase was diminished because of the relatively high mp. Insertion of an oxyphenyl unit resulted in compound **3c** and a further increase in mp by 20 K or a decrease in the I−N transition temperature by 40 K. This lowering of isotropisation temperature apparently makes the mesophases monotropic. The nematic phase remained but the SmC phase was replaced by a SmCa phase. The phenyl ring inserted is helpful for the formation of SmCa but the disturbances it brought within the overall molecular shape and therefore the molecular ordering decrease the isotropisation temperature to a great extent. When an oxystyryl unit was inserted instead (compound **3d**), a dramatic change of mesophase type was observed—a monotropic banana B_1 phase. Compared to **3c**, **3d** consists of an extra double bond. The molecular interactions are enhanced by this double bond and are helpful for the molecules to organize into an ordered phase structure (as reflected in the corresponding enthalpy changes), but the factor of bent conformation still dominates slightly. Therefore, it is a banana phase and monotropic. It is interesting to note that the values of mp and isotropisation temperatures are lower for **3d** than for **3c**. It is the opposite for **2c** and **2d**. When an extra benzoate unit was introduced, a derivative (**3e**) with a relatively wide thermal range of B_2 phase was obtained. This result indicates that the banana phase would be stabilized when the arms of the bent molecules possess large value of polarizability, the same as that observed for series **2**. It is noted that the mp is lower for **3e** than for **3d**. Introducing methoxy groups to the terminal phenyl rings resulted in compound **3f**, a formation of banana B_1 phase but with a lower mesophase temperature.

The stilbene unit is very helpful for stabilizing mesophases, either calamitic or banana mesophases. The rigidity and the conjugation of stilbene unit certainly raise the mesophase temperatures. It is interesting to note that after hydrogenation of the double bond of the stilbene unit, compounds **2e′** and **3e′** exhibit banana mesophases with lower temperatures. This result significantly indicates that an ethylene group, possessing more rotational conformations than a double bond, can be employed for linking the arms to the bending unit to obtain banana mesogens with lower mesophase temperatures. It is noted that the corresponding temperature is lower for the compound containing six phenyl rings.

Optical Observation and Electric Field Effects. *For the Nematic Phase: Unprecedented Electric-Field-Switching Behavior.* The nematic phases of compounds **2**, **3a**, and **3b** exhibit schlieren textures with 2- and 4-brush defects and resemble those of the calamitic nematic phase. A homeotropic texture developed rather easily for **2** when it was sandwiched between ITO (indium tin oxide) glasses, which is attributed to the hydrophilicity of the hydroxyl group. This homeotropic texture turned to birefringent textures when a DC electric field was applied in the direction perpendicular to the glass substrates, indicating that the anisotropy of the dielectric constant ($\Delta\epsilon$) is negative for **2**. For a homogeneously aligned (EHC cell) nematic phase of **3a**, with the alignment direction parallel to one of the crossed polarizers, a uniform dark texture with strong optical fluctuation was observed. Upon application of a low DC field (5 μm thickness and 5 V), pairwise and uniformly spaced birefringent straight stripes developed with the stripe long axis parallel to the rubbing direction, Figure 1a. The pairwise birefringent stripes turned orange and purple when the sample was rotated, images b and c of Figure 1, and the colors were exchanged with a reversing rotation. This stripe pattern disappeared at a slightly higher field and the texture showed low birefringence with weaker optical fluctuation. When the sample was then rotated, a texture of uniform color was observed and a switching between uniform colors was observed with electric field on and off, Figure 2. Similar behaviors were observed for the nematic phase of **3b**. The results of molecular calculation indicate that the directions of the net dipole moments of **3a** and **3b** make large angles with respect to the axes of main skeletons. Therefore the dielectric anisotropy is negative for **3a** and **3b**. The behaviors observed here are different from those of the well-known calamitic mesogens having either positive or negative dielectric anisotropy. Apparently the bent conformation of these molecules results in an interesting electric-field-switching behavior —a phenomenon deserving further studies.

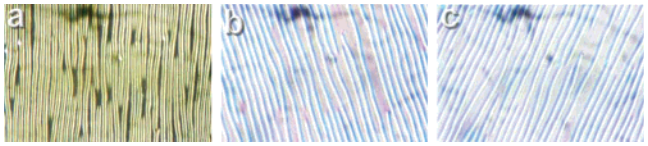


Figure 1. Textures of the nematic phase of **3a**, homogeneously aligned under electric fields at 153 °C. For 5 V/5 μm: (a) pairwise birefringent stripe pattern, (b,c) exchange of colors when the sample in (a) is rotated. The horizontal edge is 0.375 mm.

Figure 2. Homogeneously aligned nematic phase of **3a** exhibits switching of colors with electric field (a) off and on at (b) 0.8 V μm^{-1} and (c) 2 V μm^{-1} at 155 °C. Horizontal edge is 0.75 mm.

For Smectic C: 2-Brush and 4-Brush defects—Anticlinic Layer Structure. Cooling the isotropic liquid of **2a** across the phase transition, focal conic, and homeotropic textures (similar to those of calamitic SmA) appeared first and stayed for a very short temperature range. A slightly cooling of this texture resulted in a drastic change, broken focal conic developed from the focal conic areas and birefringent schlieren texture developed from the homeotropic areas. These behaviors are similar to those of the calamitic Sm A and Sm A−SmC transition, although the molecules of **2a** are considered to have a bent conformation. But it is evident that there are defects of 2- and 4-brushes in this newly

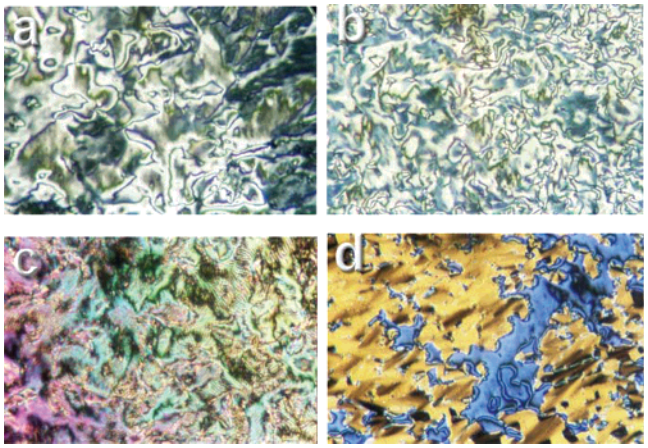


Figure 3. Photomicrographs showing textures of SmC phases of hockey stick molecules. (a) **2a**, 75 °C, schlieren texture with 2-brush defects; (b) **2b**, schlieren texture, with 2- and 4-brush defects obtained by cooling the isotropic liquid to the SmC phase, 78 °C; (c) **3a** at 146 °C, schlieren texture with transient stripes and 2-brush defects; (d) **3b** at 148.2 °C, textures of focal conic and schlieren with 2- and 4-brush defects. The horizontal edge is 0.375 mm.

developed birefringent schlieren texture, Figure 3a. These 2-brush defects distinguish this phase from that of the known calamitic SmC phase. The monotropic SmC phase of **2b** also displayed 2- and 4-brush defects (Figure 3b) but crystallized easily.

Broken focal conic accompanied with schlieren textures resembling those of calamitic SmC phase were observed when the nematic phase of **3a**, sandwiched between a microscope slide and cover slip, was cooled across the phase transition. Transient stripe patterns developed in the schlieren areas when this SmC phase was cooled, a behavior frequently observed in the calamitic SmC phase. There were defects with 2- and 4-brushes in the schlieren areas, Figure 3c. The textures of SmC of compound **3b** also displayed 2-brush defects, Figure 3d. Defects of 2-brushes have been considered as evidence for the anticlinic arrangement of the neighboring layers in the smectic phase of calamitic mesogens.[17] The above observations indicate the existence of anticlinic layer structure in the SmC phases of **2a**, **2b**, **3a**, and **3b** and represent the first example of an anticlinic layer structure of smectic phases formed by the achiral hockey stick molecules.

On the nematic phase (of **3a**) being cooled to the SmC phase, in an EHC cell (polyimide coated and rubbed for parallel alignment), there were elongated domains of various sizes with long axes parallel to the rubbing direction and with disclinations between them. The colors were the same for all the domains when the rubbing direction was parallel to the polarizer. But they were two different colors when the sample was rotated or the polarizers were decrossed, Figure 4a. The colors of these domains were exchanged when the rotation angle was reversed. When the applied DC field was increased to 10 V/5 μm, the domain colors were changed to dark brown and yellow (Figure 4b), accompanied by texture motions. These dark brown and yellow domains remained unchanged when the polarity of the electric field was reversed, but exchanged their light and dark appearances when the sample was rotated or the polarizer was decrossed. When the DC field was increased from low field to high field, the textures remained static but the dark brown domains became lighter gradually and the yellow domains became brown, Figure 4c−f. A maximal optical contrast between these domains could be obtained at a certain angle of rotation, and the same value of rotation angle was obtained in either direction. This observation indicates that the molecules are uniformly packed within each domain and tilted in the opposite directions in the neighboring domains, and the rotation angle for maximal contrast is related to the optical tilt angle of molecules of this SmC phase. The temperature dependence of this tilt angle is depicted in Figure 12 along with that evaluated from X-ray results. This tilt angle increases as the temperature is lowered away from the nematic−SmC transition temperature, reaches a maximal value, and then decreases when the SmC−SmCa transition temperature is approached.

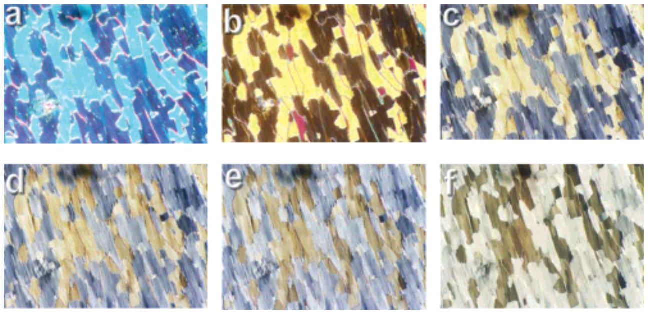


Figure 4. Photomicrographs of the SmC phase of **3a** in a cell (thickness 5 μm) with surfaces treated for homogeneous alignment under various DC electric fields. At 144 °C, aligning direction rotated by 42°: (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, and (f) 50 V. The horizontal edge is 0.375 mm.

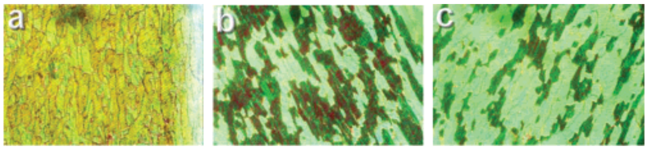


Figure 5. Textures of the lower-temperature SmC phase of **3a,** at 93 °C, showing parallel lines pointing to the opposite directions in the neighboring domains, with the sample rotated by (a) 0, (b) −24, and (c) 24°. The horizontal edge is 0.75 mm.

At a lower temperature of the SmC phase of **3a**, there were parallel lines across all the domains, Figure 5. These lines were nearly equally spaced and pointing in opposite directions for the neighboring light and dark domains (or the colored domains without a field). When the sample was rotated for the maximal contrast between the light and dark domains, the lines in the light domains were parallel to the polarizer. These observations also indicate that the molecules are tilted in opposite directions in the neighboring colored domains. Upon application of a DC field, the angle between the lines of the neighboring domains decreased gradually with increasing field strength. With a high enough electric field, the light and dark domains were replaced by domains containing stripe textures with stripe axes nearly in the same direction and meanwhile superimposed by yellow and blue colors (Figure 6). The domains exchanged their colors when

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[17] (a) Takanishi, Y.; Takezoe, H.; Fukuda, A.; Komura, H.; Watanabe, J. *J. Mater. Chem.* **1992**, *2*, 71−73. (b) Takanishi, Y.; Takezoe, H.; Fukuda, A.; Komura, H.; Watanabe, J. *Phys. Rev. B* **1992**, *45*, 7684−7689. (c) Nishiyama, I.; Goodby, J. W. *J. Mater. Chem.* **1992**, *2*, 1015−1023. (d) Lagerwall, S. T. *Ferroelectric and Antiferroelectric Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1999; pp 331−334.

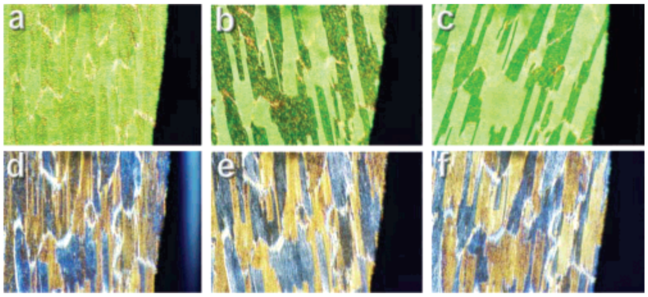

Figure 6. Textures of the lower-temperature SmC phase of **3a** (at 93 °C and 5 μm thickness) with the electric field off and a rotation angle of (a) 0, (b) −10, and (c) 19°, and an electric field of 20 V and a rotation angle of (d) 0, (e) −6, and (f) 8°. The horizontal edge is 0.375 mm.

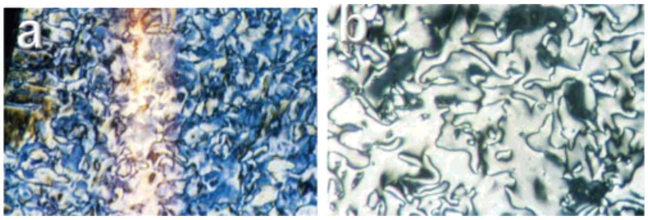

Figure 7. Photomicrographs showing schlieren textures of 2-brush defects for the anticlinic smectic C phases (SmCa): (a) **3a**, 84.1 °C; (b) **3c**, 118.4 °C. The horizontal edge is 0.375 mm.

the sample was rotated to the other direction. These parallel lines were restored upon removal of the electric field. The time for restoration of these lines was proportional to the field strength and inversely to the temperature.

A peak of response current has been observed for this phase under a triangular wave of electric field; the value of spontaneous polarization evaluated was on the order of 10 nC/cm^2. However, we were not sure that the ionic species did not come into play even after several attempts. A thorough study is still needed.

For SmCa: Anticlinic Smectic C Formed by Bent Molecules. Drastic texture changes were observed when the SmC phase of **3a**, sandwiched between nontreated glasses, was cooled across the phase transition. The schlieren texture of SmC was swept by a new schlieren texture containing plenty of 2-brush defects[17] (Figure 7a). The optical appearance across this schlieren texture was more uniform than that of SmC phase. There were floating liquids sweeping through the sample, a behavior easily observed during temperature variation. Some periodic parallel stripes, rather similar to the pitch band observed for chiral smectic phases, occurred in the broken focal conic areas and some thicker schlieren areas (see Figure 8). These behaviors resemble the typical phase transitions of ferroelectric SmC to antiferroelectric SmC observed for chiral calamitic mesogens.[17] On the isotropic phase of **3c** (monotropic N and SmCa phases) being cooled, schlieren and homeotropic textures appeared and stayed for a short temperature range and then drastically turned to a new schlieren texture with defects mostly of 2-brushes (Figure 7b). The occurrence of, or the tendency to develop, the 2-brush defects is easier for **3c** than for **3a**. One possible reason for this difference is that the preceding phase is a nematic for **3c**, and the other reason is because of the molecular shape. Comparing the bent shape of **3a** and **3c** hockey stick molecules, the benzoate moiety in the short arm of **3c** makes this arm more like a calamitic mesogen and results in a phase structure more like the anticlinic arrangement of two calamitic smectic layers. These observations indicate that the phase obtained also consists of an anticlinic arrangement of molecular layers formed by these achiral hockey stick molecules. It is noted that the enthalpy change values for SmC−SmCa of **3a** and N−SmCa of **3c** transitions are 0.02 and 1.59 kJ/mol, respectively.

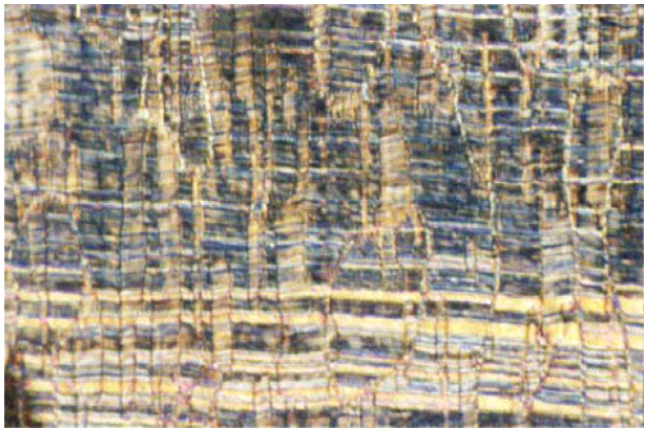

Figure 8. Photomicrograph showing the growth of parallel lines (horizontal) overlapped on the domains of SmC phase of **3a** when the sample was cooled to the SmCa phase. The horizontal edge is 0.75 mm.

On the SmC phase of **3a** being cooled to the SmCa in an EHC cell, periodic parallel lines start to grow from the boundaries of the domains (Figure 8). They wriggled parallelly through all domains, across the boundaries, and gradually took over all of the SmC areas. The rate of growth depended on the cooling rate. During the growth of these wriggle lines textures, the electric field effect was obvious in the remaining SmC areas but only a slight variation was observed in the wriggle lines areas (up to a field of 40 V for 5 μm thickness).

When this SmCa phase was subjected to a triangular wave of electric field, a response current peak was obtained and the value of spontaneous polarization was on the order of 50 nC/cm^2. Resolving the response current into separate peaks was unsuccessful under the ultimate conditions of our instrument, 2 Hz and 70 V (peak to peak) for 5 μm.

Banana Phases Formed by Unsymmetrically Bent Molecules. Typical textures of banana phases were observed for B_1 of **3d** and **3f**, banana-leaf-like textures, and for B_2 of **2e** and **3e,** grainy textures. The banana-leaf-like textures did not respond to the applied electric field. The textures of B_2 obtained by cooling the isotropic liquid of compound **2e** with a DC field are shown in Figure 9. A slight rotation of the extinction cross and obvious birefringence changes are observed by switching the electric fields, indicating a homochiral SmC_AP_A property according to the classification of Link et al.[2] There are two response current peaks for the B_2 phase of **2e** and **3e** for each half-cycle of the applied triangular wave of electric field, indicating an antiferroelectric behavior (Figure 10). The peak areas correspond to a spontaneous polarization of 668 nC/cm^2 at 121 °C and 539 nC/cm^2 at 135 °C for **2e** and **3e**, respectively. It is evident from these observations that banana phases can be stabilized when the arms of the hockey stick (or bent) molecule possess

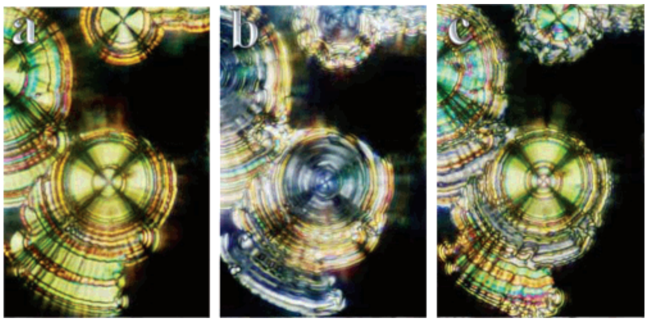

Figure 9. Texture changes of the B_2 phase of **2e**, with a rotation of the extinction cross by the electric field at 128 °C of (a) +5, (b) 0, and (c) −5 V/μm.

large enough polarizability to enhance molecular interaction and thus stabilize the layer structure.

X-ray Study

Powder X-ray diffraction was carried out for a sample packed in a capillary. Cooling the isotropic liquid of compound **3a** to the nematic phase, we observed a broad peak in the small-angle region and a broad band in the wide-angle region (Figure 11). The broad peak corresponds to a value of 47.74 Å and is taken as the molecular length in the nematic phase. Throughout the SmC phase, a strong and sharp peak in the small-angle region and a broad band in the wide-angle region were observed; a typical run is shown in Figure 11. The *d*-spacing value of the phases as a function of temperature is shown in Figure 12. The *d*-spacing drops drastically at temperatures just below the N−SmC transition and then increases steadily when the temperature is decreased further. The corresponding tilt angle as a function of temperature is also shown in Figure 12. The tilt angle increases as the temperature is lowered, reaches a maximum, and then decreases gradually on further cooling. The variation of tilt angle as a function of temperature resembles that estimated from the optical observation but with some discrepancies in the upper range of the SmC phase. This discrepancy is attributed to the optical behavior mainly being dominated by the aromatic core, which assumes a different tilt angle from the molecule as a whole. Across the transition to the SmCa phase, a pattern similar to those of SmC phase is obtained (85 °C; Figure 11). The sharp peak in the small-angle region indicates a simple layered structure and the broad band in the wide-angle region indicates liquidlike behavior within the layer. The sharp peak corresponds to a periodicity of 43.9 Å, larger than that of the SmC phase. This could be due to a smaller tilt angle or changes of molecular conformation.

The X-ray diffraction patterns for the banana phases of hockey stick molecules **2e** and **3e** are shown in Figure 13. A sharp peak in the small-angle region (the small peak at ~4° 2θ is due to the Kapton tape) and a broad band in the wide-angle region are observed for the B_2 phase of compound **2e**. The sharp peak corresponds to a layer spacing of 39.6 Å and indicates a simple layered structure for this B_2 phase. The distance between the two terminal carbon atoms of this bent molecule is 49.36 Å, as calculated by HyperChem 5.01 AM1. These values yield a tilt angle of 36.6°. A similar pattern is obtained for compound **3e** except that a second-order peak is observed in the small-angle region. These peaks correspond to a layer spacing of 40.6 Å and indicate a tilt angle of 45.6° given the molecular length 57.98 Å (by HyperChem 5.01 AM1). For compound **3f**, the X-ray pattern resembles that of the typical B_1 phase, two sharp peaks in the small-angle region and a broad band in the wide-angle region. The sharp peaks correspond to a rectangular lattice of size 38.9 Å × 25.6 Å.

Chemical Computation

Chemical computation was carried out for the molecules obtained in the processes of molecular structure modifications in order to obtain the corresponding molecular properties such as molecular conformation, molecular length, and the associated net dipole moment. Molecular geometry was optimized by AM1 of HyperChem 5.01; the molecular conformation and the molecular length were then obtained, and the corresponding dipole moment was calculated and located by Molecular Mechanics MM+ accordingly. In general, a bent conformation was obtained when a long segment was attached at the position meta to the carbon−carbon double bond of the main skeleton. The bending angles of these molecules are not constant but range from 100 to 130°, and there seems to be no simple correlation between the bending angle and segment attached. Nevertheless, these results agreed quite well with the observed thermodynamic results as manifested by the lowering of the isotropisation temperature and narrowing of the mesophase temperature range. This agreement gave us some confidence for accepting the results of molecular length and dipole moment; some of the results are listed in the Supporting Information. It deserves a note that for all the bent molecules studied here, along the main skeleton, the plane of the benzoate unit(s) is not coplanar with that of the stilbene moiety, and the dipole moments are located in the direction with a large angle with respect to the main skeleton (of both three- and four-ring skeleton systems). These results indicate that the anisotropies of the dielectric constant of these bent molecules are negative and agree with the electric field effects observed for compounds **2**, **3a**, and **3b**. It is noted further that for all the hockey stick molecules studied, the corresponding dipole moments are out of the plane containing the bent skeletons. This orientational relationship maybe one of the reasons that the electric field effects of these molecules are different from those of calamitic mesogens.

Discussion

It is a general observation that attachment of a substituent lateral to a rodlike mesogen results in destabilization of the mesophase and manifests in lowering and narrowing the mesophase temperature and range. The results presented here agreed well with this expectation, as can be seen from the results of compounds **1**−**2d** and compounds **3a**−**c**. Insertion of phenyl rings would certainly increase the interactions between molecules and hence stabilize the mesophase as well as increase the corresponding temperatures. This is particularly true when the insertion is located along the main skeleton, as revealed by the results of three- and four-ring molecules carrying the same lateral substituents. If a phenyl ring or a benzoate unit is inserted in the lateral direction, the mesophase would occur only when the molecular interaction forces and the stabilization factor are strong enough to overcome the destructing factors—bent conforma-

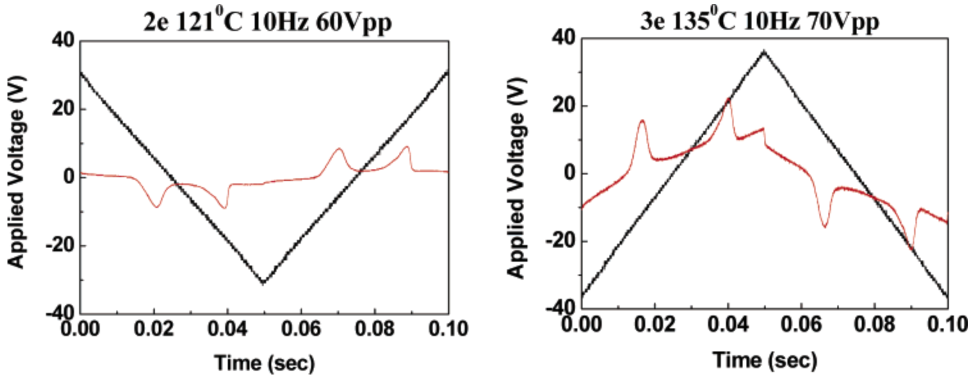

Figure 10. Antiferroelectric behavior for the banana phases of **2e** and **3e** under a triangular wave of the electric field.

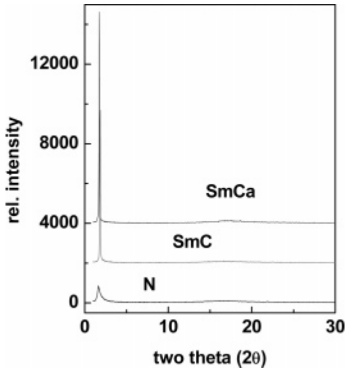

Figure 11. X-ray diffraction patterns for powder sample of the phases of **3a.**

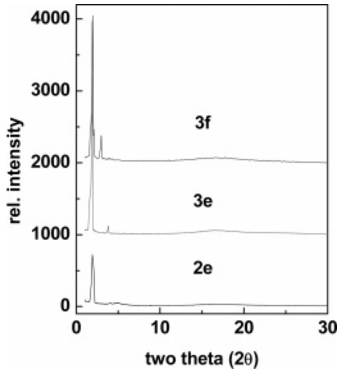

Figure 13. X-ray diffraction patterns for the powder sample of the banana phases of compounds **2e**, **3e**, and **3f**.

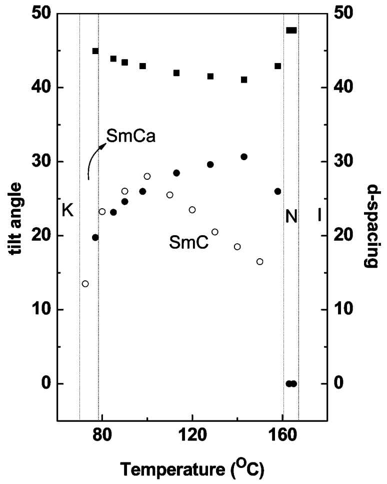

Figure 12. Tilt angle and *d*-spacing as a function of temperature for **3a** estimated by X-ray and optical measurements. Closed square, *d*-spacing; closed circle, tilt angle by X-ray; open circle, tilt angle by optical observation.

tion and steric hindrance. When the stabilization factor is contributed mainly by the main skeleton, a hockey-stick-type mesogen is obtained, e.g., **3a**−**c**. When contributions from both the main and lateral wings are considerable, a banana mesogen is obtained, even though the two wings are different in length, e.g., **2e** and **3e**. The bent conformation and the dipole moments and polarizability associated with the moieties employed play the central roles for the variation of mp and isotropisation temperatures and determine the mesophase to be enantiotropic, monotropic, or even vanishing. The variation of mesophases accompanied the structural modification studied here follows this observation. The results presented here indicate that the occurrence of anticlinic arrangement of neighboring layers is a consequence of bent molecular conformation. Furthermore, the anticlinic layer structure constitutes an intermediate phase between the calamitic smectic and banana mesophases.

Williams domains[18] occur as stripe patterns when a calamitic nematic mesogen of negative dielectric anisotropy and positive conductivity anisotropy is subjected to a DC electric field with a voltage below a certain threshold value. Above this threshold value, the domains disappear and turbulence sets in. The stripe axes are in the direction perpendicular to the direction of the originally aligned director. The stripe patterns observed for the nematic phases of the bent molecules studied here have stripe axes parallel to the aligning direction. These stripes disappeared at a slightly higher voltage; no turbulence was observed, even at a much higher voltage, and uniform color was observed instead. This behavior strongly indicates that all three axes of the bent molecules are aligned under high field strength. These behaviors distinguish this nematic phase from that of the known calamitic nematic phases.[19] This is attributed to the bent conformation of the molecules. It deserves further studies and will be reported later.

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(18) (a) de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Oxford University Press: New York, 1993. (b) Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H. W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1998.

(19) (a) Prasad, V.; Kang, S. W.; Suresh, K. A.; Joshi, L.; Wang, Q. B.; Kumar, S. *J. Am. Chem. Soc.* **2005**, *127*, 17224−17227. (b) Acharya, B. R.; Primak, A.; Kumar, S. *Phys. Rev. Lett.* **2004**, *92*, 145506. (c) Madsen, L. A.; Dingemans, T. J.; Nakata, M.; Samulski, E. T. *Phys. Rev. Lett.* **2004**, *92*, 145505. (d) Görtz, V.; Goodby, J. W. *Chem. Commun.* **2005**, 3262−3264. (e) Pelzl, G.; Eremin, A.; Diele, S.; Kresse, H.; Weissflog, W. *J. Mater. Chem.* **2002**, *12*, 2591−2593.

The optical appearances of the schlieren textures of the SmC and SmCa phases of these bent molecules, and the transition between them, are similar to those of the corresponding phases of calamitic mesogens, but with the following distinct differences. The schlieren textures of SmC phases of these bent molecules are distinguished from those of the calamitic SmC phase in that there are 2-brush defects, domains of opposite tilt angle, and the electric-field effects. These 2-brush defects strongly suggest the existence of anticlinic arrangements of neighboring smectic layers. This is reasonable because the constituting molecules have bent conformation, and this conformation persists in this mesophase as manifested in the lowering and narrowing of the mesophase temperature and range. The drastic texture changes across the transition between the SmC and SmCa (compound **3a**) clearly indicate that the phase structures are different, although the DSC thermogram displayed only a small enthalpy value. For the calamitic mesogens, the long axes are synclinic in the SmC phase and anticlinic in the SmCa phase. The optical features of the schlieren and the broken focal conic textures strongly suggest that the phases of these bent mesogens also contain the corresponding phase structures. This is probably true, because the optical birefringence is primarily due to the main skeleton containing the stilbene moiety. The hydrocarbon chain (**3a**) connected at the meta position played only a minor role in this birefringence, but certainly affected the tilt of the molecular directors as well as the phase structure. Thus, being a bent conformation in a tilt smectic phase formation of 2-brush defects is therefore possible. Hence, the phase structure is tentatively called a quasianticlinic layer structure in order to distinguish it from that of the known anticlinic smectic C (SmCa). Enhancing the interactions between neighboring molecules by incorporating more polarizable moieties, such as phenyl rings, in the short arms will make the anticlinic smectic phase more likely to occur from **3a** to **3c**. When the interactions are strengthened to such a great extent, a banana phase will be formed even for arms with different lengths, from **3a** to **3d** and **3e**.

The formation of domains with opposite tilt angle and different optical features is also closely related to the bent conformation as well as the conformational isomers because of the rotation of benzoate unit(s) contained in the main skeleton. The molecules studied here can be considered to be comprised of three segments, i.e., stilbene unit, benzoate unit(s), and the substituent at the meta-position. The stilbene unit is known to have phenyl rings coplanar with the central double bond in the trans conformation in most of the cases and is considered to be rather rigid structurally. The benzoate unit(s), including the ester linkage, is capable of rotating with respect to the phenyl ring of stilbene via the phenyl-O single bond. The dipole moment associated with the ester linkage is therefore rotated accordingly. The net dipole moment for the hockey stick molecules discussed here is contributed primarily by those associated with the ester linkage(s). The direction of the dipole moment of the ester linkage apparently makes a large angle with respect to the long axis of the main skeleton. This would result in negative dielectric anisotropy. The results of chemical calculation and the observed electric field effects are consistent with this consideration. The long substituent at the meta position plays the major role in making the resulting molecule into a bent conformation as manifested in the corresponding thermodynamic results. The dipole moment associated with this substituent partially, depending on the type of linkage, cancels those from the main skeleton. When the compound is cooled to the temperature at which molecules are packed to form the corresponding phase, the rotational motions of the benzoate unit(s) are partially frozen. Molecules are packed together with the same conformation and form a domain consisting of molecules of the same tilt.

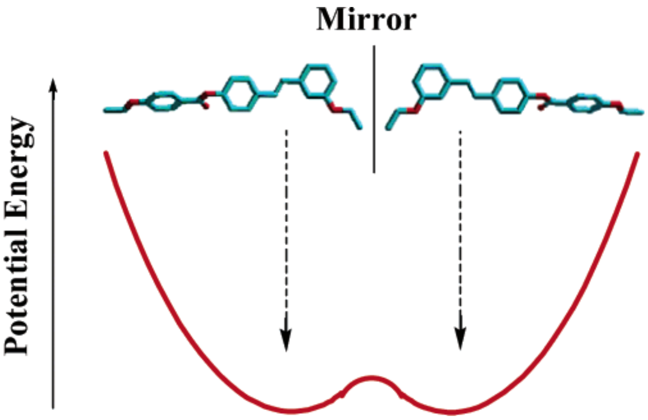

Figure 14. Doubly degenerate case formed by the mirror images of conformational isomers of the hockey stick molecule shown with schematic representations.

Molecular calculation indicates that the plane of benzoate unit makes an angle of 20−50° with respect to the plane of the stilbene moiety depending upon the bent molecules studied. It can be envisaged that a reversing rotation of the benzoate unit would result in a mirror image conformation but with the same energy. These conformational isomers are chiral and constitute a doubly degenerate case (Figure 14). The occurrence of domains of opposite tilts have the same probabilities, as observed in the sizes and numbers of these domains, agrees with this consideration.

These types of conformational isomers have been considered to be the causes for several mesophase behaviors observed experimentally: the helical phase structure of banana phases originated from the opposite twists of benzoate units attached to the central bent unit, on the basis of ^{13}C NMR results;[20] chiral phases formed, and also could be induced, by a typical rodlike phenyl ester because of its twist.[21] The occurrence of the SmCa phase of a hockey stick mesogen was ascribed to the rotation of the phenyl ring of Schiff's base moiety[10b] and the induction of the SmCa phase in rodlike mesogens by achiral dopants with a branching tail.[22] Considering these observations, the formation of an equal number of domains with opposite tilts is considered to originate from the conformational isomers discussed above.

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(20) Sekine, T.; Niori, T.; Sone, M.; Watanabe, J.; Choi, S. W.; Takanishi, Y.; Takezoe, H. *Jpn. J. Appl. Phys., Part 1* **1997**, *36*, 6455−6463.

(21) Kajitani, T.; Masu, H.; Kohmoto, S.; Yamamoto, M.; Yamaguchi, K.; Kishikawa. K. *J. Am. Chem. Soc.* **2005**, *127*, 1124−1125.

(22) Thisayukta, J.; Samulski, E. T. *J. Mater. Chem.* **2004**, *14*, 1554−1559.

The electric field applied for the changes observed for SmC of **3a** (images a and b of Figure 4) seems to be a characteristic field. Similar field strength was obtained for compound **3b**. This field strength varied very slightly across the entire SmC phase and exhibited a feature that resembled the temperature dependence of the *d*-spacing observed in the X-ray study. These color changes were accompanied by texture motions, and the texture motions were caused by the process of aligning the molecular dipoles to the applied field—a threshold field. From then on, the textures remained static, the optical fluctuation was much weaker, and the transmitted intensity was lower. Apparently the molecular motions are restricted by the field applied, and the molecular optical axes are tipped slightly toward the light path. This behavior is similar to that observed for the nematic phase, i.e., all three molecular axes are aligned, except that the phase here has layered structures. An obvious change of birefringence with field strength is noted, but it remains to be clarified if it is related to the biaxiality of the dielectric.[11a] Although the field effects are rather obvious, we were unable to obtain a definite conclusion regarding the existence of spontaneous polarization for this SmC phase after several attempts. It deserves further study.

The parallel lines occurring within the already existing domains for the lower-temperature SmC is apparently related to the smectic layers (Figure 5). The tilt angle measured by the optical method matched that from X-ray, unlike those for the upper range of the SmC phase. The DSC thermogram did not show any trace of phase transition throughout the entire SmC phase. It is not clear whether these parallel lines are related to the *d*-spacing of this SmC phase or if they originated from a possible domination of one of the conformational isomers. Orientations of these lines were obviously affected by the electric field applied (Figure 6). Because they were superimposed on the domain textures, it made the textures become more complicate under the electric field. The colors of the pattern were different from that observed for the upper-range SmC phase and could very possibly be due to the temperature dependence of birefringence.

The results of the DSC study showed a very small enthalpy change (0.02 kJ/mol) across the SmC–SmCa (**3a**) phase transition. This small value has been observed frequently for the corresponding phase transition of calamitic mesogens and has been considered an indication of a weakly first-order phase transition.[23] The drastic texture changes also agreed with this characteristic transition.[24] The X-ray results showed similar diffraction patterns, simple layered structures, for both SmC and SmCa phases but with an increase of 1.1 Å in *d*-spacing. There are many possible causes for this change, synclinic–anticlinic variation, changes in bending angle and tilt angle, rotation of constituting moieties, and freezing of internal motions. It could also be a combination of these factors.

Conclusion

Mesophases of nematic, smectic C and anticlinic smectic C were obtained for compounds comprised of hockey stick molecules—bent molecules with two arms different in length. The polarizability, dipole moment, and conformation of the moiety contained in the arms play essential roles in the intermolecular interactions and hence determine the existence of mesophases. The bending effect is manifested in the mesophase stability and results in the occurrence of 2-brush defects for the smectic C phases. The formation of domains with opposite tilts in the SmC phase originated from the conformational isomers of the bent molecules. The anticlinic arrangement of molecular layers comprised of these bent molecules indicates that anticlinic smectic phases are the intermediate mesophases between the conventional calamitic and banana mesophases. Because of the bent conformation and the associated dipole moment, the mesophases of these hockey stick molecules exhibit different behaviors under electric fields as compared to the corresponding calamitic phases. Banana B_2 phases comprised of hockey stick shape molecules can be stabilized when the polarizability of the moieties contained in the arms is great enough.

Acknowledgment. This work was supported by the National Science Council under Contracts NSC93-2113-M-032-006 and NSC94-2113-M-032-005.

Supporting Information Available: Details of synthetic procedures and analytical data of compounds, *d*-spacing, molecular conformation, and orientation of dipole moment. This material is available free of charge via the Internet at http://pubs.acs.org.

CM060459D

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(23) Nishiyama, I.; Goodby, J. W. *J. Mater. Chem.* **1993**, *3*, 149–159.
(24) Goodby, J. W.; Patel, J. S.; Chin, E. *J. Mater. Chem.* **1992**, *2*, 197–207.