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Nematic Liquid Crystals with Bent-Rod Shapes: Mesomorphic Thiophenes with Lateral Dipole Moments

Keiki Kishikawa, Michele C. Harris, and
Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

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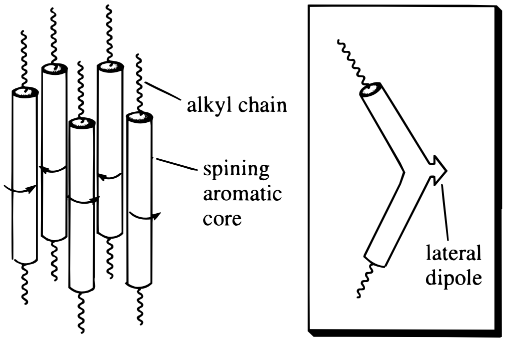
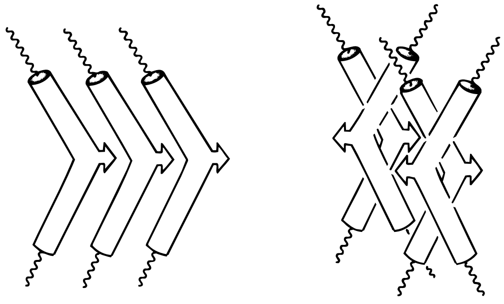
The simplest and most technologically important liquid crystal phase is the nematic.[1] Thermotropic nematic liquid crystals are generally optically uniaxial materials composed of rigid rods or disks that undergo rapid rotation, to give a uniformly disordered orientation along one axis (Scheme 1a). In an effort to discover new nematic phases, which potentially have biaxial optical properties, we are interested in bent-rod structures with lateral dipoles (Scheme 1b). Rotation of a bent-rod structure about its long axis will require a larger displacement of neighboring molecules and thereby increase the rotational activation barrier relative to a rod mesogen. The addition of lateral dipoles also has the potential to produce head-to-tail ferroelectric organization, as in a MacMillan type smectic-C structure (Scheme 1c),[2] or arrange in an antiferroelectric dimerized structure (Scheme 1d). The dipolar effects in both cases should promote biaxiality with preferential molecular orientations perpendicular to the long axis of the mesogen.

Scheme 1



(a) Organization of typical straight-rods

(b) Bent-rod with a lateral dipole



(c) Head-to-tail ferroelectric organization

(d) Antiferroelectric dimers

Bent-rod structures have recently received considerable attention due to the discovery by Takezoe of a new class of achiral ferroelectric liquid crystals.[3a] While the origins of the ferroelectric polar domains displayed by these materials are still under investigation, there is the possibility that molecules in a given domain spontaneously adopt a single chiral conformation.[3] Although a number of other related structures have been synthesized,[4] at present there is only one bent-rod structure type that has been demonstrated to display this novel ferroelectric behavior. Biaxial nematics have been the subject of numerous investigations and scientific controversy.[5] The nearest neighbor interactions shown in Scheme 1 (c and d), if supported in a nematic or smectic liquid crystal phase, should promote biaxiality. While the structures and interactions necessary to create stable liquid crystalline phases from bent-rod systems are not fully understood, it has been generally found that materials with severely bent structures display liquid crystalline phases with lower thermodynamic stability than their straight-rod relatives.[4h] To produce a bent-rod structure with good prospects for liquid crystallinity, we have decided to focus on materials with a thiophene as a central element of the mesogen. A 2,5-substituted thiophene moiety exhibits a larger angle than other logical building blocks (154° for 2,5-disubstituted thiophene, 143° for 2,5-disubstituted furan, 141° for 2,5-disubstituted pyrrole, and 120° for 1,3-disubstituted benzene), some of which have been investigated previously in bent-rod mesogenic units.[4] An additional attractive aspect of thiophene is that it exhibits a very diverse chemistry, thereby allowing for the efficient preparation of numerous derivatives. The present report details our investigations of a series of bent-rod thiophene-based liquid crystals, which systematically probe both the nature of the side chains and also the effect of lateral dipole moments on the stability of the liquid crystalline phases.

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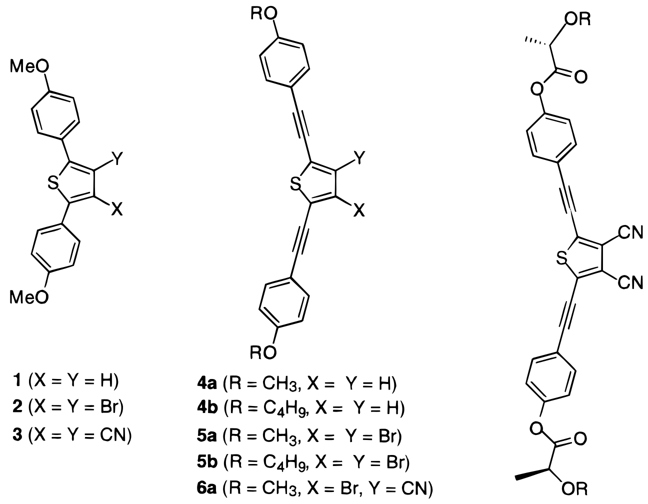
Scheme 2



1 (X = Y = H)
2 (X = Y = Br)
3 (X = Y = CN)

4a (R = CH_3, X = Y = H)
4b (R = C_4H_9, X = Y = H)
5a (R = CH_3, X = Y = Br)
5b (R = C_4H_9, X = Y = Br)
6a (R = CH_3, X = Br, Y = CN)
6b (R = C_4H_9, X = Br, Y = CN)
7a (R = CH_3, X = Y = CN)
7b (R = C_4H_9, X = Y = CN)

8a (R = C_4H_9)
8b (R = $C_{10}H_{21}$)

Scheme 3

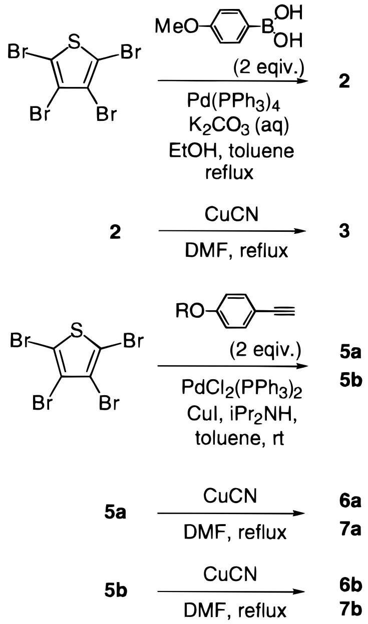


Table 1. Phase Behavior of Thiophene Derivatives[a]

Compound	Behavior
1	K $\xrightarrow{224.2\ (61.4)}$ I; K $\xleftarrow{177.8\ (-53.5)}$ N $\xleftarrow{219.5\ (-0.8)}$ I
2	K_1 $\xrightarrow{122.2\ (1.9)}$ K_2 $\xrightarrow{167.3\ (33.1)}$ I; K_1 $\xleftarrow{111.4\ (-36.0)}$ I
3	K $\underset{184.6\ (-78.5)}{\overset{216.9\ (37.5)}{\rightleftarrows}}$ I
4a	K_1 $\xrightarrow{85.5\ (-1.4)}$ K_2 $\xrightarrow{100.1\ (3.7)}$ K_3 $\xrightarrow{119.7\ (22.7)}$ N $\underset{150.5\ (-1.3)}{\overset{152.5\ (1.3)}{\rightleftarrows}}$ I; K_1 $\xleftarrow{61.6\ (-32.2)}$ N
4b	K $\underset{75.7\ (-18.8)}{\overset{94.3\ (23.0)}{\rightleftarrows}}$ N $\underset{158.4\ (-1.9)}{\overset{161.3\ (1.8)}{\rightleftarrows}}$ I
5a	K $\xrightarrow{147.6\ (25.7)}$ I; K $\xleftarrow{134.3\ (-26.6)}$ N $\xleftarrow{143.2\ (-0.7)}$ I
5b	K_1 $\xrightarrow{91.3\ (9.0)}$ K_2 $\xrightarrow{93.7\ (-14.9)}$ K_3 $\xrightarrow{111.3\ (35.7)}$ N $\underset{133.3\ (-1.5)}{\overset{135.7\ (1.4)}{\rightleftarrows}}$ I; K_1 $\xleftarrow{60.3\ (-29.1)}$ N
6a	K_1 $\xrightarrow{163.6\ (-5.2)}$ K_2 $\xrightarrow{174.5\ (28.8)}$ I; K_1 $\xleftarrow{154.7\ (-23.9)}$ N $\xleftarrow{167.0\ (-0.5)}$ I
6b	K $\underset{98.8\ (-35.4)}{\overset{138.0\ (38.7)}{\rightleftarrows}}$ N $\underset{143.5\ (-1.0)}{\overset{145.9\ (0.9)}{\rightleftarrows}}$ I
7a	K $\xrightarrow{205.3\ (40.7)}$ I; K $\xleftarrow{173.6\ (-31.6)}$ N $\xleftarrow{178.6\ (-0.3)}$ I
7b	K $\underset{150.8\ (-88.6)}{\overset{180.3\ (48.7)}{\rightleftarrows}}$ I

[a] The transition temperatures (°C) and enthalpies (in parenthses, kJ/mol) were determined by DSC (10 °C/min) and are given above and below the arrows. **K**, **K_1**, **K_2**, and **K_3** indicate crystal phases, and N and I indicate nematic and isotropic phases, respectively.

A range of mesogenic cores (**1**−**8** in Scheme 2) were synthesized using related palladium-catalyzed cross-coupling protocols. The synthetic procedures, as shown in Scheme 3, all begin with a bromonated thiophene and the first step is palladium-catalyzed cross-coupling at the most reactive 2,5-positions of thiophene. Preparation of **2** requires a chemoselective Suzuki coupling with tetrabromothiophene and a phenyl boronic acid derivative.[6] Further substitution of the remaining bromides of **2** with copper(I) cyanide gives **3**.[7] Similar chemoselective Sonogashira coupling[8] with 4-alkoxyphenylacetylene moieties gives series **5**, which can be carried on to give series **6** and **7**. Compounds **1**, **4a**, and **4b** were prepared by analogous coupling reactions with 2,5-dibromothiophene. Removal of the two methyl groups in **7a** using BBr_3[9] followed by esterification with lactic acid analogues[10] gives **8a** and **8b**.

The phase behavior of all the materials investigated is shown in Table 1. Compounds **1**,[15] **2**, and **3** display the smallest aspect ratio and limited liquid crystallinity. Compound **1** displays a monotropic nematic phase at high temperature. The addition of bromide and nitrile substituents destabilizes the nematic phase and compounds **2** and **3** are not liquid crystalline. A cursory investigation of small amounts of related materials with X = H, Y = CN, and X = Br, Y = CN also showed no evidence of liquid crystallinity.

Increasing the aspect ratio of a mesogen generally increases its tendency to form a liquid crystalline phase. Hence, we find a greater stability of the liquid crystal-

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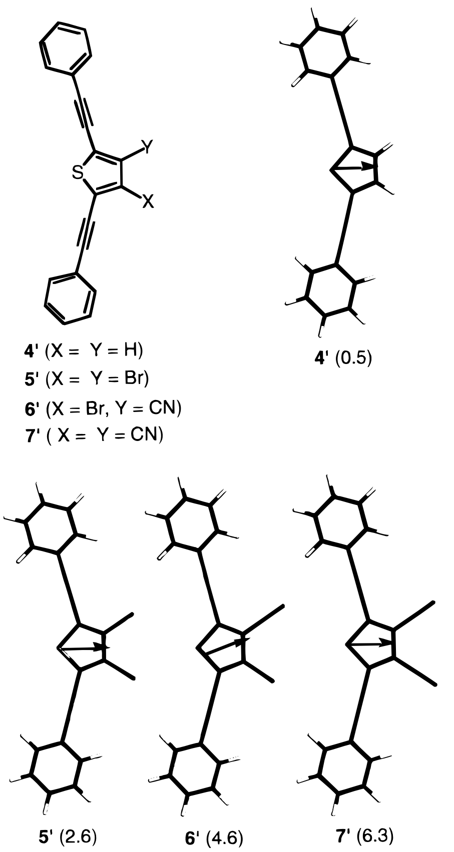

Figure 1. Optimized molecular geometries and calculated dipole moments (in parentheses) for **4′**, **5′**, **6′**, and **7′**.

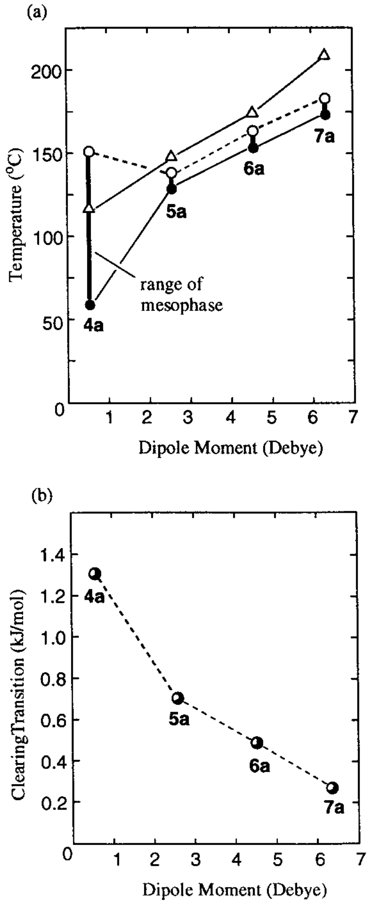

Figure 2. The effect of the dipole moment on the transition temperatures and transition enthalpies. (a) Plot of the transition temperature against the dipole moment: Melting point, △; isotropic−nematic transition (on cooling), ○; crystallization point (on cooling), ●. (b) Plot of the clearing transition against the dipole moment.

line phases for series **4**−**7**. We observe an enantiotropic mesophase for the methoxy derivative **4a**. In the butoxy analogue, **4b**, the mesophase range is expanded and interestingly has a higher (8 °C) clearing point. The fact that the nematic phases of **4a** and **4b** have considerably wider stability confirms the greater tendency of the extended mesogens toward liquid crystallinity. We again find that adding the bromide and nitrile groups lowers the mesophase stability. In the methoxy compounds **5a**, **6a**, and **7a** we observe only monotropic nematic phases with a narrow range of stability. The nematic behavior is slightly more robust for two of the butoxy analogues, and **5b** and **6b** both retain enantiotropic characteristics with a reduced range of stability relative to **4b**. Compound **7b**, in contrast to **7a**, is not a liquid crystal.

A principle concern is to understand if the dominant effect of the bromide and nitrile groups on the stability of the liquid crystalline phase is due to their dipoles or simply by their physical size. To quantify the molecular dipoles, AM1 calculations[11] were performed on a model mesogen without the terminal alkoxy functionality (Figure 1) and on two isomeric structures both of which have terminal methoxy groups. The terminal alkoxy groups complicate the dipolar considerations since the oxygen moiety presents a substantial molecular dipole. Depending upon the conformation, the alkoxy can either oppose or reinforce a dipole associated with the central thiophene ring. The molecular dipole of the dinitrile mesogen **7a** is at a maximum of 9 D when the oxygens adopt a crescent conformation. The isomer of the same molecule (**7a**) with opposing oxygen contributions produces a 4 D dipole. Considering the dipolar differences between the two isomeric forms allows us to deduce that the lateral dipole of the core without the contribution of the terminal oxygens is approximately 6.5 D. This number compares very favorably with the 6.3 D calculated for the simplified model **7′** without the terminal alkoxy groups. As expected, the electron-donating ability of the oxygens increases the dipole moment of the central thiophene ring (push−pull effect) by a small amount. By considering model compounds **4′**−**7′**, which do not have the alkoxy group, we avoid these conformational complications and focus only on the central lateral dipole.

As can be seen for the four model structures in Figure 1, the lateral central dipole increases considerably when the hydrogens (**4′**) on the thiophene are changed to bromides (**5′**). Further substitution with nitrile groups (**6′** and **7′**) results in a much larger dipole.

Qualitative comparisons of the phase behavior of the compounds exhibit clear correlations to the lateral dipole moment. This is particularly apparent from the trends in the methoxy analogues shown in Figure 2a. We find that the melting point and the liquid crystalline transition temperatures (cooling) both scale with the lateral central dipoles of **4a**, **5a**, **6a**, and **7a**. While the dipoles associated with the alkoxy groups are likely important, we have used the assumption that the contribution of these groups will be constant in the series. Considering that our goal is to determine the

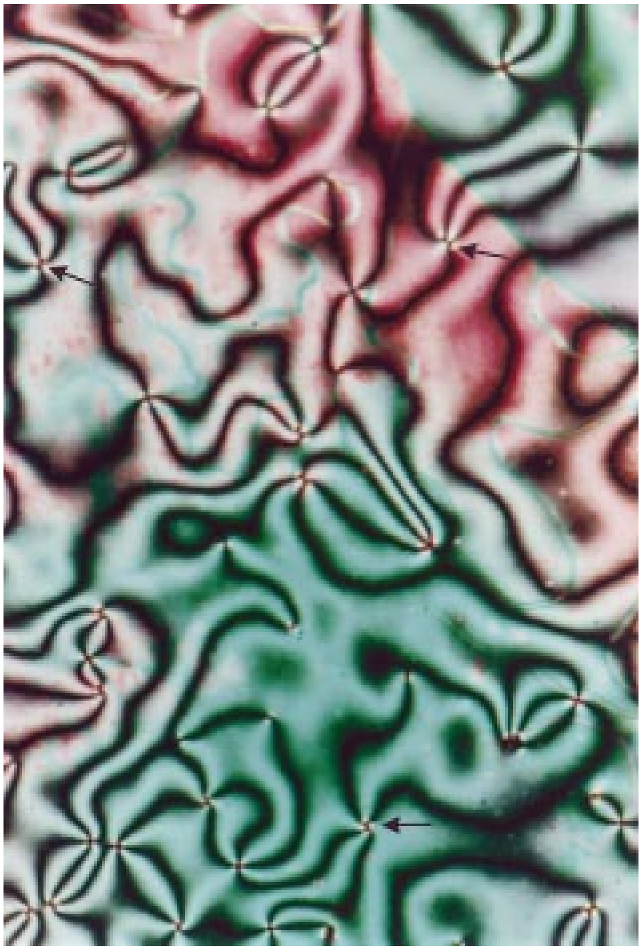

Figure 3. Optical texture showing two brush disclination pairs (examples marked with an arrow), as well as the two- and four-brush disclinations for the nematic phase of **5a** at 141 °C.

qualitative trend as this lateral dipole increases, this assumption seems acceptable. Another interesting trend shown in Figure 2b is the magnitude of the isotropic-to-mesophase transition enthalpy versus lateral dipole moment. In this case a dramatic decrease in enthalpy is observed with increasing dipole moment, indicating that high lateral dipoles produce liquid crystal phases with an entropy more like their isotropic phases.

The optical textures of nematic liquid crystals are an important diagnostic for the presence of a biaxial phase.[5a] It has been proposed that the elastic constants of a biaxial nematic should produce only two-brush patterns. However, it is important to note, that these patterns must be observed in a sample that avoids surface effects. The present materials exhibit a dominance of two-brush disclinations with four-brush disclinations having high birefringence around the singularity point. Additionally in all the compounds having high lateral dipoles (X = Y = CN, Br) (Figure 3), there are a number of two-brush disclination pairs that appear to be pinned in close proximity to each other. Freely suspended films that give a surface-free preparation could not be prepared due to the high transition temperatures of these compounds. However the presence of four-brush disclinations precludes the possibility that these compounds are biaxial nematics. Nevertheless, the textures do suggest a strong pinning to the glass surface, which produces the pairs of two-brush disclinations and the high birefringence around some disclinations. This strong pinning may be simply due to strong chemical bonding to the surface or be the result of the organization of the molecules around point charges. With regard to this last point, it is important to note that bent molecules with large lateral dipoles have been predicted by Meyer to display large flexoelectric coefficients.[12] The dipoles of a flexoelectric liquid crystal should spontaneously produce an electric field when bent. The presence of charges at a surface could cause the molecule to have a similar arrangement.

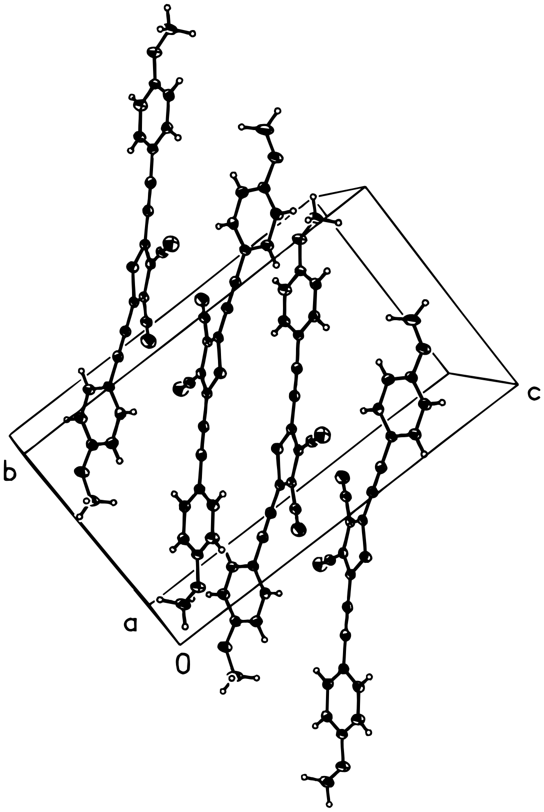

Figure 4. X-ray structure of **7a** (ORTEPs shown at 30% probability).

On the basis of a single X-ray structure of **7a** shown in Figure 4,[13] the antiparallel arrangement of lateral dipoles shown in Scheme 1d seems most likely. In this structure the molecules adapt a relatively planar structure with opposing and slightly offset dipoles. The fact that such organizations are also used in Meyer's flexoelectric prediction also suggests that these materials should exhibit a significant flexoelectric effect.

Conclusion

In summary, we have investigated a new class of nematic liquid crystals with a range of lateral dipoles. Bent-rod liquid crystals are potential biaxial nematics and are also related to the recently discovered ferroelectric banana phases.[2] Large flexoelectric coefficients may provide strong surface anchoring and thereby be useful for the design of bistable displays.[14] It does not appear that any of the compounds exhibit a biaxial nematic phase. Future studies will be directed at expanding this structural class of bent-rod-like mesogens and will attempt to find compounds with greater thermodynamic stability and biaxiality in their nematic phases.

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Supporting Information Available: Synthetic details for the compounds discussed and X-ray data for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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