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Liquid-Crystalline Compounds Consisting of Two Mesogenic Cores in Parallel Conformation

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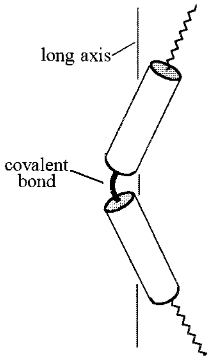
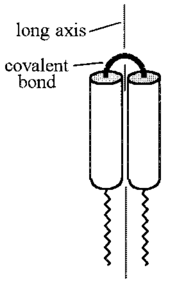
In recent years, arrangement of two mesogens along a long axis with an angle by using a covalent bond (bent-rod shapes, (A) in Scheme 1) has brought about a breakthrough in producing novel phenomena in liquid-crystal phases, such as modulated smectic phases by twin liquid-crystalline dimers,[1] antiferro- and ferroelectric phases by achiral banana-shaped molecules,[2,3] or antiparallel organization in mesophases by bent-rod molecules with a central large dipole.[4] Those highly ordered mesophases originate because of hindered rotation of the bi-mesogenic molecules around their long axes. On the other hand, however, it is difficult to realize a stable mesophase because the hindered rotation reduces conformational mobility and leads to crystallization easily.[5] In this paper, we describe synthesis, behaviors, and organization of liquid-crystalline compounds **1** and **2**, and this is the first example of liquid-crystalline dimers consisting of two mesogenic units in

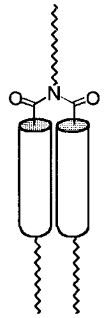
Scheme 1. Arrangement of Two Mesogenic Cores in Liquid-Crystalline Compounds



(A) Arrangement of two mesogens along the long axis



(B) Arrangement of two mesogenic cores in parallel conformation



(C) Two mesogenic cores connected by an iminodicarbonyl moiety

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(3) Ferroelectric phase by achiral bent-rod molecules: (a) Walba, D. M.; Körblava, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. *Science* **2000**, *288*, 2181. (b) Walba, D. M.; Körblova, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. *J. Phys. Org. Chem.* **2000**, *12*, 830. (c) Walba, D. M.; Körblova, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Clark, N. A. In *Liquid crystal materials and devices*; Bunning, T., Chen, S., Chien, L.-C., Kajiyama, T., Koide, N., Lien, S.-C., Eds.; Materials Research Society: San Francisco, 1999; Vol. 559, pp 3−14. (e) Walba, D. M.; Körblova, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Clark, N. A. In *Liquid Crystals III*; Khoo, I.-C., Ed.; SPIE: Denver, CO, 1999; Vol. 3800, pp 21−28.

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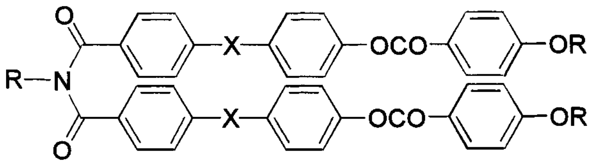
(5) Instability of bent-rod molecules: Cai, R.; Samulski, E. T. *Liq. Cryst.* **1991**, *9*, 617.

10.1021/cm010023s CCC: $20.00

Table 1. Phase Behavior of Compounds 1, 2, and 3b



1a : X = CH_2CH_2, R = C_4H_9
1b : X = CH_2CH_2, R = C_8H_{17}
2a : X = OCO, R = C_4H_9
2b : X = OCO, R = C_8H_{17}
3b : X = CC, R = C_8H_{17}

Compound	Behavior
1a	Crystal $\xrightarrow{135\ (4.5)}$ Isotropic $\xrightarrow{115\ (-^{b})}$ N $\xrightarrow{114\ (-4.5)}$ Crystal
1b	Crystal $\underset{48\ (-5.6)}{\overset{114\ (9.0)}{\rightleftharpoons}}$ SmA $\underset{142\ (-2.6)}{\overset{145\ (2.9)}{\rightleftharpoons}}$ Isotropic
2a	Crystal $\underset{129\ (-5.7)}{\overset{145\ (5.7)}{\rightleftharpoons}}$ N $\underset{176\ (-0.045)}{\overset{176\ (0.045)}{\rightleftharpoons}}$ Isotropic
2b	Crystal $\underset{71\ (-3.1)}{\overset{98\ (3.1)}{\rightleftharpoons}}$ SmA $\underset{193\ (-2.3)}{\overset{199\ (2.4)}{\rightleftharpoons}}$ Isotropic
3b	Crystal $\underset{144\ (-8.5)}{\overset{155\ (9.5)}{\rightleftharpoons}}$ Isotropic

[a] The transition temperatures (°C) and enthalpies (in parentheses, kcal/mol) were determined by DSC (5 °C)/min) and are given above and below the arrows. "N" and "SmA" indicate nematic and smectic A phases, respectively. [b] The enthalpy was not measured because of the unstable monotropic nematic phase.

parallel conformation in which their edges are connected by a curved junction ((B) in Scheme 1).[6]

In preceding papers,[7] large angles of two mesogens in arrangement (A) were applied to liquid-crystalline molecules to realize stable mesophases. In our design, the two mesogens are arranged parallel to the long axis (B) in which rotation of the molecule around its long axis is less hindered to realize the stable mesophase. To realize structure (B), an iminodicarbonyl moiety was selected as the central connector (C). Electrostatic repulsion between the two carbonyl-oxygen atoms and intramolecular attractive aromatic−aromatic interactions between the cores arrange the two mesogens in parallel conformation.[8]

The behaviors of the liquid-crystalline compounds **1** and **2** were depicted in Table 1.[9] Compound **1a** ($R^1 = R^2 = C_4H_9$, X = CH_2CH_2) showed unstable monotropic nematic phase at 115 °C only upon rapid cooling, while **2a** ($R^1 = R^2 = C_4H_9$, X = COO) showed stable enantiotropic nematic phase at 145−176 °C upon heating. The viscous nematic phase may have a highly aligned structure because it showed different textures from those in other nematic phases. Only a few four-brush disclinations with very thin lines were observed, and

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(6) Liquid-crystalline dimers where the mesogenic units are locked more or less parallel to each other: (a) Thurmes, W. N.; Wand, M. D.; Vohra, R. T.; Crandall, C. M.; Xue, J.; Walba, D. M. *Liq. Cryst.* **1998**, *25*, 149. (b) Walba, D. M.; Dyer, D. J.; Sierra, T.; Cobben, P. L.; Shao, R.; Clark, N. A. *J. Am. Chem. Soc.* **1996**, *118*, 1211. (c) Walba, D. M.; Dyer, D. J.; Chen, X. H.; Müller, U.; Cobben, P.; Shao, R.; Clark, N. A. *Mol. Cryst. Liq. Cryst.* **1996**, *288*, 83. (d) Stevens, F.; Dyer, D. J.; Müller, U.; Walba, D. M. *Langmuir* **1996**, *12*, 5625. (e) Walba, D. M.; Dyer, D. J.; Cobben, P. L.; Sierra, T.; Rego, J. A.; Liberko, C. A.; Shao, R.; Clark, N. A. In *Thin Films for Integrated Optics Applications*; Wessels, B. W., Marder, S. R., Walba, D. M., Eds.; Materials Research Society: San Francisco, 1995; Vol. 392, pp 157−162.

(7) For example: (a) Kossmehl, G.; Hoppe, F. D. *Liq. Cryst.* **1993**, *15*, 383. (b) Iglesias, R.; Serrano, J. L.; Sierra, T. *Liq. Cryst.* **1997**, *22*, 37. (c) Neumann, B.; Joachimi, D.; Tschierske, C. *Liq. Cryst.* **1997**, *22*, 509. (d) Artzner, F.; Veber, M.; Clerc, M.; Levelut, A.-M. *Liq. Cryst.* **1997**, *23*, 27. (e) Semmler, K. J. K.; Dingemans, T. J.; Samulski, E. T. *Liq. Cryst.* **1998**, *24*, 799. (f) Lin, H.-C.; Shiaw, J.-M.; Liu, R.-C.; Tsai, C.; Tso, H.-H. *Liq. Cryst.* **1998**, *25*, 277. (g) Nozary, H.; Piguet, C.; Tissot, P.; Bernardinelli, G.; Bünzli, J.-C. G.; Deschenaux, R.; Guillon, D. *J. Am. Chem. Soc.* **1998**, *120*, 12274.

(8) Photoreaction of iminodicarbonyl derivatives: (a) Kohmoto, S.; Kobayashi, T.; Nishio, T.; Iida, I.; Kishikawa, K.; Yamamoto, M.; Yamada, K. *J. Chem. Soc., Perkin Trans. 1* **1996**, 529. (b) Kishikawa, K.; Akimoto, S.; Yamamoto, M.; Kohmoto, S.; Yamada, K. *J. Chem. Soc, Perkin Trans. 1* **1997**, 77.

(9) For details regarding the synthesis of **1a**, **1b**, **2a**, and **2b**, see the Supporting Information.

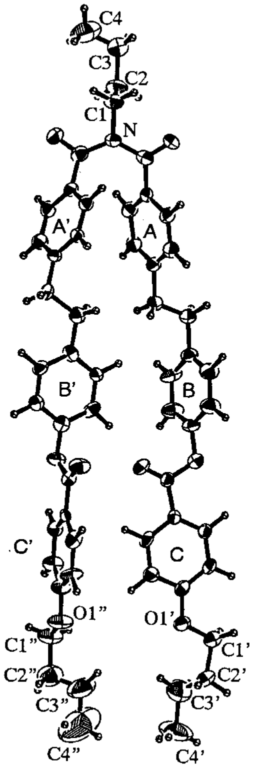
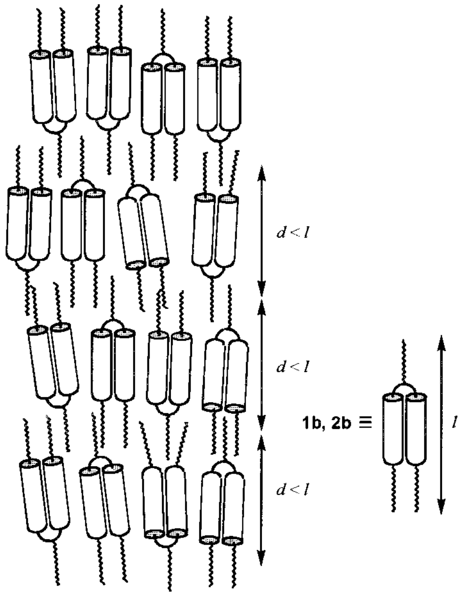


Figure 1. X-ray structure of **1a**; ORTEPs shown at 30% probability.

the boundary of the homeotropic and homogeneous areas was kept clearly for a couple of minutes. The transition enthalpy at the transition from the nematic to the isotropic phase (N−I transition) was extremely small (0.045 kcal/mol) and the peak was sharp in DSC. After the N−I transition (176 °C) until 210 °C upon heating, pushing on the glass plate (not to give a thermal shock from an iron wire) caused flashing of the liquid sample and recovery of the nematic phase was observed; the nematic phase disappeared within 1−10 s after removal of the pressure. The phenomenon was also observed in the nematic phase of 4-cyano-4′-octylbiphenyl, but only at a narrow temperature range, from 40 °C (N−I transition temperature) to 41 °C. In powder X-ray diffraction of **2a** in the nematic phase at 150 °C, one broad peak at a small angle (30.2 Å) and two small broad peaks at large angles (6.7 and 4.8 Å) were observed. The length, 30.2 Å, is slightly shorter than the molecular length (31 Å) in the molecular modeling, which indicates ordered alignment of molecules in direction of the long axis.

Both compounds **1b** ($R^1 = R^2 = C_8H_{17}$, $X = CH_2CH_2$) and **2b** ($R^1 = R^2 = C_8H_{17}$, X = COO) showed only smectic A phases with broad temperature ranges (**1b** 114−145 °C, **2b** 98−199 °C upon heating) in which typical textures of smectic A, bâtonnets, fanlike, and homeotropic textures were observed, respectively. Conoscopic study of the smectic A phase of **2b**, which was aligned homeotropically between two glass plates treated with 1,1,1,3,3,3-hexamethyldisilazan, indicated that the mesophase was a uniaxial smectic A phase. Further, to confirm the importance of flexibility of the mesogenic units in liquid crystallinity, behavior of acetylene derivative **3b** ($R^1 = R^2 = C_8H_{17}$, X = CC), which has two rigid straight rod units, was investigated; however, any liquid-crystal phase was not observed.

Scheme 2. Layer Structure of 1b and 2b with Overlapping of the Alkyl Chains (Side View, *d* = Layer Distance, *l* = Molecular Length)



Compound **1a** was recrystallized from ethyl acetate−methanol to give its single crystals and X-ray crystallography was performed to investigate conformation of the molecule in the crystal phase.[10] The molecule has its two mesogens in slightly twisted parallel conformation (Figure 1). Intramolecular face-to-edge arrangements were observed between aromatic rings B and B′ and between C and C′ because of CH/π interaction.[11] The three butyl groups do not have all-trans conformations, but gauche conformations around their C2−C3, C1′−C2′, and C1″−C2″ bonds (dihedral angles: C1−C2−C3−C4, −81°; O1′−C1′−C2′−C3′, 61°; O1″−C1″−C2″−C3″, −64°), respectively. The gauche conformation may be better to minimize the molecular volume in the crystal packing. Further, it was found that the molecules formed antiparallel dimers.

To investigate layer structures of the liquid-crystal phase of **1b** and **2b**, X-ray diffraction was performed. In smectic A phases of **1b** (130 °C) and **2b** (110 °C), the layer distances 32.1 and 33.4 Å were observed as (100) peaks, distances 16.0 and 16.9 Å were also observed as (200) peaks, and shoulders were at the left side of the (100) peaks, respectively. In the case of **2b**, the shoulder at 38.7 Å was distinguishable from the (100) peak. From molecular modeling (Chem3D[12]), the molecular lengths are 42 Å for both **1b** and **2b**. The layer distances are 10 and 8.5 Å shorter than those molecular lengths, respectively. Accordingly, more than a half length of the *n*-octyl group is overlapping between layers of the smectic A phases.

The following mechanism was postulated for organization of the liquid-crystal phases. The small and sharp peaks of **1a** and **2a** in DSC (4.5 and 5.7 kcal/mol for melting (or crystallization)) and the broad small-angle

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[10] For details regarding the X-ray crystal structure of **1a**, see the Supporting Information.

[11] CH/π interaction: Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665. Edge-to face: Paliwal, S.; Geib, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 4497.

[12] Molecular modeling of compounds **1** and **2** was carried out by Chem3D (Cambridge software corporation).

peak in the nematic phase (30.2 Å ≈ molecular length of **2a**) indicate no large conformational change in the transitions. Time-averaged dimers generate in an antiparallel manner to cancel the strong dipole of the iminodicarbonyl moiety of each molecule, which makes the nematic phase of **2a** highly oriented and recoverable by applying pressure. In the case of **1b** and **2b**, the cross section of an excluded volume of the *N*-alkyl chain is rather small compared with that of the two core parts. The overlap of the alkyl chains between layers may originate in supplying the spatial lack of alkyl chains of the iminodicarbonyl moiety. (Scheme 2) This type of overlap of alkyl chains was also observed in the smectic A phase of a swallow-tail liquid-crystalline compound as one part of the structure.[13] However, in our system, interdigitation of molecules is the main layer structure of the smectic A ($d < l$), and an ordinary layer distance ($d \approx l$) for the smectic A phase also existed.

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Supporting Information Available: Synthesis of **1**, **2**, **3**, **4**, **6**, and **7**, X-ray structure report of **1a**, and charts of powder X-ray diffraction of **1b**, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Interdigitation in swallow-tail liquid-crystalline compounds: Diele, S.; Manke, S.; Weissflog, W.; Demus, D. *Liq. Cryst.* **1989**, *4*, 301.