Synthesis, Crystal Structures and Mesomorphic Properties of Liquid Crystals with a *N*, *N*′-Bis(tropon-2-yl)piperazine Skeleton

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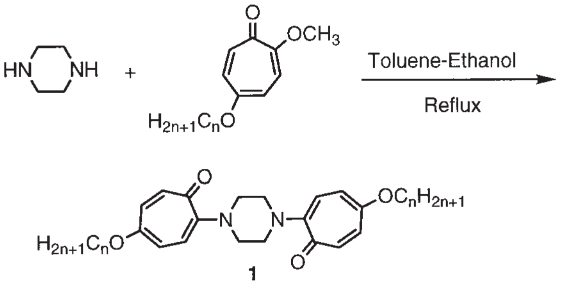
New troponoid liquid crystals with a *N*, *N*′-bis(tropon-2-yl)piperazine core were prepared. *N*, *N*′-Bis(tropon-2-yl)piperazine derivatives (**1**) had a smectic C phase with lower thermal stabilities than the corresponding benzenoid derivatives (**2**), which had a smectic B phase. A single crystal of **1d** had distinct layer structures observed in a smectic C phase.

Synthesis, elucidation of crystal structures, and investigation of physical properties of new liquid crystals are important for studying the relationship between molecular structures and mesophases. Recently we have prepared liquid crystals with tropolone core[1–6] since the tropolone core has a large dipole moment (3.5 D),[7] which would help to form layer. We investigated the crystal structures and mesomorphic properties of liquid crystals (**1**) with a bis(tropon-2-yl)piperazine core to compare with those of the benzenoids **2**,[8] whose precise phases were not determined.



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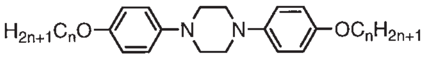
n=4, 6, 8, 10, 12, 14, 16, 18



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N, *N*′-Bis(5-alkoxytropon-2-yl)piperazines (**1**) were prepared by the condensation of piperazine and the corresponding 5-alkoxy-2-methoxytropone in an ethanol-toluene solution.[9] The structures and purities of **1** were ascertained by NMR spectroscopic data and elemental analysis. The transition temperatures and thermal behaviors of the textures were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage as well as X-ray diffraction study.

The thermal behaviors of troponoids and the corresponding benzenoids are summarized in Table 1. Troponoids (**1**) and benzenoids (**2**) had different mesomorphic sequences. The former series had a phase sequence of crystals-smectic C-isotropic for n = 8–16, while the latters had a phase sequence of crystals-smectic B-isotropic. The smectic phases were determined from the following observation as well as from the X-ray diffraction studies, i.e., bâtonnets, fan and schlieren textures for smectic C phase; homeotropic and natural textures for smectic B phase. As shown in Table 1, troponoids (**1**) showed smectic phases with lower thermal stabilities than the corresponding benzenoids (**2**). This is due to the wider molecular width of the seven-membered ring compared with the benzenoid ring.[10]

Table 1. Transition temperatures (°C) and transition enthalpies (kJ·mol^{-1}) of **1** and **2**

	n	1	2[8]
a	4	Cr·164·Iso	Cr·197·S_B·227·Iso
b	6	Cr·162·Iso	Cr·172·S_B·218·Iso
c	8	Cr·136(45.9)·[S_C·113[a]·]Iso	Cr·163·S_B·203·Iso
d	10	Cr·133(43.0)·[S_C·121[a]·]Iso	Cr·161·S_B·189·Iso
e	12	Cr·117(69.9)·S_C·128(10.5)·Iso	—
f	14	Cr·122(94.8)·S_C·127(8.4)·Iso	—
g	16	Cr·127(134.3)·[S_C·124[a]·]Iso	—
h	18	Cr·127·Iso	—

Cr, crystals; S_C, smectic C phase; S_B, smectic B phase; Iso, isotropic liquid; [ ] = monotropic.
[a]Transistion detected only by polarized optical microscopy.

The molecular and crystal structures of **1b** and **1d** are shown in Figures 1 and 2.[11] Interestingly, both adopt a zig-zag conformation. Compound **1d** formed a tilted layer structure such as a smectic C phase, while compound **1b** did not form any layer structures as observed in **1d**.

Furthermore, we measured the X-ray diffraction pattern of the mesophases. The smectic layer spacing (*d*) of **1e** was observed to be 32.9 Å (118 °C) for the smectic C phase. The *d* of **2a** was observed to be 25.7 Å (215 °C) for the smectic B phase. The calculated molecular lengths (*l*) of **1e** and **2a** by the MM2 method were 44.9 Å and 25.4 Å, respectively. The *d*/*l* ratio of the smectic B phases of **2a** was 1.01, which suggested that the molecules were orthogonal to the layer. On the other hand, the *d*/*l* ratio of the smectic C phases of **1e** was 0.73 (118 °C). The reason why

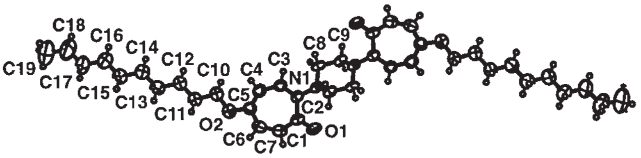

Figure 1. Molecular structure of **1d**.

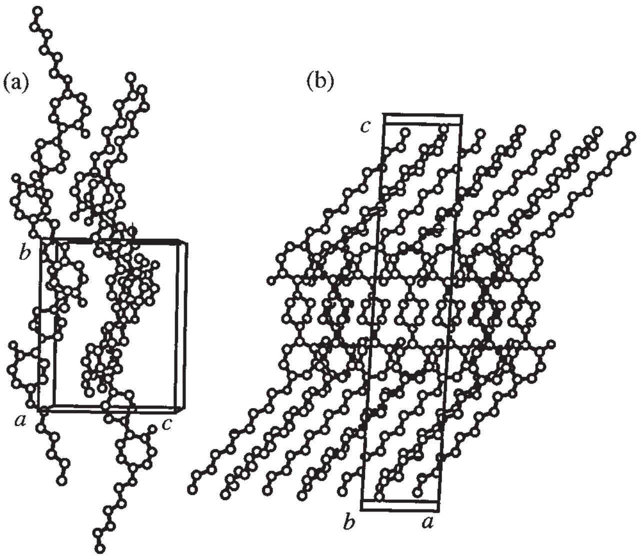

Figure 2. Crystal structures of (a) **1b** viewed down the *a* axis and (b) **1d** viewed down the *b* axis.

compound **1e** tilted with respect to the layer normal would be explained by the alignment of the outboard dipole moment of **1** as shown in Figure 3, where the dipole moments aligned consistently in opposite directions. The tilt angle of **1e** was 43.1 ° (118 °C), which was larger than that [**1d**: 30 °] obtained by X-ray crystallographic analysis.

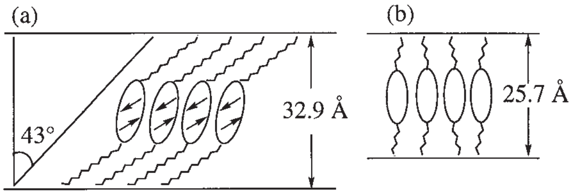

Figure 3. Packing medels of (a) **1e** in the smectic C phase and (b) **2a** in the smectic B phase.

Thus, a *N*, *N*′-bis(tropon-2-yl)piperazine core with the outboard dipole moments should be useful to form the tilted layered structure. The crystal structure of **1d** was closely related to the layer structure of smectic C phase, whereas that of **1b** was not. In order to form a layer structure, the length of the alkyl side chains required to the more than 8 at least.

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References and Notes

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9 Synthetic details and physical data will be reported elsewhere. Elemental analyses. **1a**; Found: C, 71.11; H, 7.77; N, 6.30%. Calcd for $C_{26}H_{34}N_2O_4$: C, 71.21; H, 7.81; N, 6.39%. **1b**; Found: C, 72.69; H, 8.46; N, 5.63%. Calcd for $C_{30}H_{42}N_2O_4$: C, 72.84; H, 8.56; N, 5.66%. **1c**; Found: C, 74.01; H, 9.08; N, 4.84%. Calcd for $C_{34}H_{50}N_2O_4$: C, 74.14; H, 9.15; N, 5.09%. **1d**; Found: C, 75.06; H, 9.84; N, 4.58%, Calcd for $C_{38}H_{58}N_2O_4$: C, 75.21; H, 9.63; N, 4.62%. **1e**; Found: C, 75.86; H, 9.97; N, 4.13%. Calcd for $C_{42}H_{66}N_2O_4$: C, 76.09; H, 10.03; N, 4.23%. **1f**; Found: C, 76.76; H, 10.34; N, 3.87%. Calcd for $C_{46}H_{74}N_2O_4$: C, 76.83; H, 10.37; N, 3.90%. **1g**; Found: C, 77.26; H, 10.60; N, 3.46%. Calcd for $C_{50}H_{82}N_2O_4$: C, 77.47; H, 10.66; N, 3.61%. **1h**; Found: C, 77.87; H, 10.97; N, 3.30%. Calcd for $C_{50}H_{82}N_2O_4$: C, 78.02; H, 10.91; N, 3.37%.

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11 Crystal data for **1b**: $C_{30}H_{42}N_2O_4$, monoclinic, $P2_1/n$, $a = 8.0767$ (6) Å, $b = 15.0020$ (13) Å, $c = 11.7796$ (8) Å, $\beta = 97.704$ (2)°, $V = 1414.41$ (19) Å^3, $Z = 2$, $M_r = 494.66$, $D_x = 1.161\ \mathrm{mg{\cdot}m^{-3}}$, refinement on F^2 (SHELXL97),[12] $wR(F^2) = 0.0710$. Crystal data for **1d**: $C_{38}H_{58}N_2O_4$, monoclinic, $P2_1/a$, $a = 6.8361$ (6) Å, $b = 7.4795$ (7) Å, $c = 35.137$ (3) Å, $\beta = 92.410$ (2)°, $V = 1795.0$ (3) Å^3, $Z = 2$, $M_r = 606.86$, $D_x = 1.123\ \mathrm{mg{\cdot}m^{-3}}$, refinement on F^2 (SHELXL97),[12] $wR(F^2) = 0.2800$.

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