Synthesis and Mesomorphic Properties of Liquid Crystals with a 5,5'-Bitropolone Skelton

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New troponoid liquid crystals with a bitropolone core were prepared. The ester derivatives (**1**) had enantiotropic smectic A and/or C phases with higher thermal stabilities than the corresponding benzenoid derivatives (**2**), which had smectic B phases. X-ray diffraction studies revealed that the layer spacings of the smectic A and C phases were not so much different.

Recently we have prepared troponoid liquid crystals with a tropone core such as 5-hydroxytropolone,[1] 5-aminotropolone,[2] 2-amino-5-hydroxytropone,[3] 5-cyanotropolone,[4] and 2-amino-5-phenyltropone.[5] The tropolone core has a large dipole moment (3.5 D),[6] which would help to form a layer structure. The cores enhanced formation of smectic phases when compared with the corresponding benzenoids. In benzenoid liquid crystals, a biphenyl unit has been widely used as one of the most useful cores.[7] Although biphenol derivatives (**2**)[8] have been reported to be smectogens, their precise phases were not determined. In this paper, the mesomorphic properties of 5,5'-bitropolone compounds are investigated to compare with those of the benzenoids **2**.
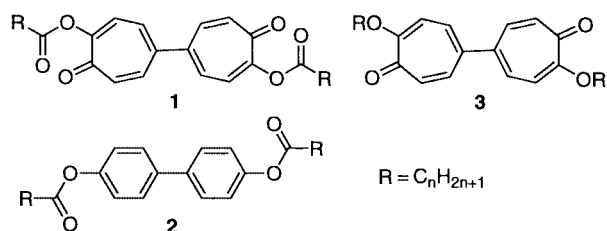
5,5'-Bitropolone was obtained by homocoupling reactions of 5-iodotropolone in the presence of [Pd(PPh₃)₄].[9] Reaction of 5,5'-bitropolone with alkanoyl chloride or alkyl bromide in a triethylamine–HMPA solution afforded the bitropolone derivatives (**1** and **3**).[10] The benzenoid derivatives (**2**)[8] were prepared by esterification of 4,4'-biphenol with alkanoyl chloride. 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 bitropolones and the corresponding benzenoids are summarized in Table 1. Troponoids (**1**) and benzenoids (**2**) have different mesomorphic sequences. The former series had a phase sequence of crystals–smectic A–isotropic for n = 7 and crystals–smectic C–smectic A–isotropic for n = 8–15, while the latter series have 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, focal-conic fan, and homeotropic textures for smectic A phase; broken-fan and schlieren textures for smectic C phase; homeotropic and mosaic textures for smectic B phase. As shown in Table 1, troponoids (**1**) showed smectic phases with higher thermal stabilities than the corresponding benzenoids (**2**). This is due to the presence of the carbonyl group. On the other hand, the ether derivatives such as 2,2'-dihexyloxy- and 2,2'-didecanyloxy-5,5'-bitropones were not mesomorphic (**3a**; Cr·141.3·I, **3b**; Cr·141.4·I).

The molecular and crystal structures of **1c** and **2a** are shown in Figure 1.[11] The crystals of **1c** and **2a** have distinct layer structures such as smectic phases.
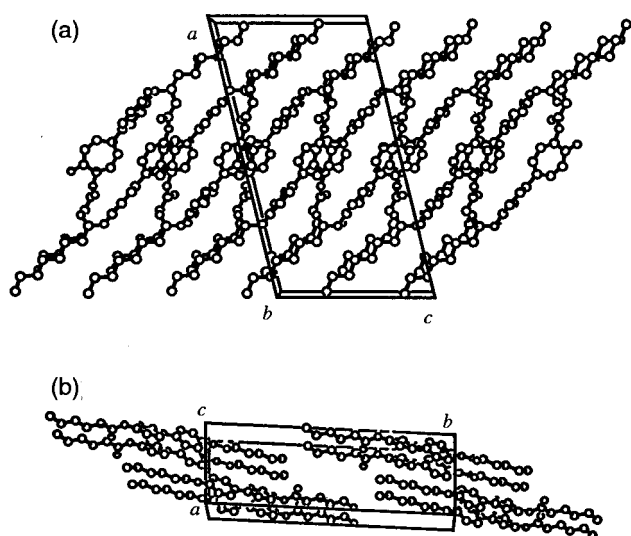
Furthermore, we measured the X-ray diffraction pattern of the mesophases. The smectic layer spacings (d) of **1i** were observed to be 35.6 Å (140 °C) for the smectic A phase and 36.5 Å (120, 125, and 130 °C) for the smectic C phase, respectively. The d of **2d** was observed to be 28.3 Å (105 and 110

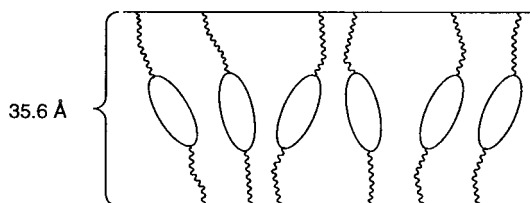R = CₙH₂ₙ₊₁

Table 1. Transition temperatures of **1** and **2**

	n	Transition temp. / °C		n	Transition temp. / °C
1a	5	Cr · 143.0 · I	**2a**	5	Cr · 117.0 · S_B · 118.0 · I
1b	6	Cr · 138.0 · I	**2b**	6	Cr · 105.0 · S_B · 118.0 · I
1c	7	Cr · 129.6 · S_A · 132.2 · I	**2c**	7	Cr · 95.0 · S_B · 122.0 · I
1d	8	Cr · 117.2 · S_C · 119.8 · S_A · 148.3 · I	**2d**	8	Cr · 95.0 · S_B · 121.0 · I
1e	9	Cr · 120.9 · S_C · 126.6 · S_A · 155.2 · I	**2e**	9	Cr · 98.0 · S_B · 122.0 · I
1f	10	Cr · 119.2 · S_C · 129.8 · S_A · 156.7 · I	**2f**	10	Cr · 100.0 · S_B · 121.4 · I
1g	11	Cr · 124.3 · S_C · 128.2 · S_A · 157.2 · I	**2g**	11	Cr · 101.1 · S_B · 120.8 · I
1h	12	Cr · 110.0 · S_C · 123.3 · S_A · 152.5 · I	**2h**	12	Cr · 102.1 · S_B · 120.4 · I
1i	13	Cr · 110.2 · S_C · 125.2 · S_A · 146.1 · I	**2i**	13	Cr · 102.0 · S_B · 118.2 · I
1j	14	Cr · 115.0 · S_C · 131.8 · S_A · 151.6 · I	**2j**	14	Cr · 105.3 · S_B · 118.9 · I
1k	15	Cr · 118.2 · S_C · 131.6 · S_A · 153.4 · I	**2k**	15	Cr · 119.0 · I

Cr, crystals; S_A, smectic A phase; S_C, smectic C phase; S_B, smectic B phase; I, isotropic liquid.

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

°C) for the smectic B phase. The calculated molecular lengths (*l*) of **1i** and **2d** by the MM2 method are 43.6 Å and 31.4 Å, respectively. The *d/l* ratios of the smectic A and C phases of **1i** are 0.82 and 0.84, respectively. Although it seems to be unusual that both are almost the same and the former smectic A has rather a smaller *d/l* ratio than the latter, the value (0.82) is typical for smectic A phases,[12] where terminal chains deform and cores randomly tilt to make molecules orthogonal to the layer planes as shown in Figure 2. In the case of the smectic C phase, the molecules had an organized tilt direction to the normal to the layer planes, where mobility of the terminal chains would be reduced. As a result, the layer spacings between the smectic A and C phases were not so much different with each other.

Figure 2. Packing model of **1i** in the smectic A phase. Terminal alkyl chains deformed and bitropolone cores randomly tilted.

Thus, a bitropolone core should be more useful to enhance the thermal stabilities of liquid crystalline states than a biphenyl core. Packing models of compounds **1** and **2** were consistent with the observation of the single crystallographic analyses.

References and Notes

1 A. Mori and H. Takeshita, *J. Synth. Org. Chem. Jpn.*, **53**, 197 (1995); A. Mori, H. Taya, M. Uchida, and H. Takeshita, *Chem. Lett.*, **1996**, 699; A. Mori, S. Takematsu, and H. Takeshita, *Chem. Lett.*, **1997**, 1009; A. Mori, H. Taya, H. Takeshita, and S. Ujiie, *J. Mater. Chem.*, **8**, 595 (1998); A. Mori, H. Takeshita, R. Mori, S. Takematsu, M. Takemoto, and S. Ujiie, *Liq. Cryst.*, **28**, 171 (2001).

2 A. Mori, H. Takeshita, R. Nimura, and M. Isobe, *Liq. Cryst.*, **14**, 821 (1993).

3 A. Mori, K. Hirayama, N. Kato, H. Takeshita, and S. Ujiie, *Chem. Lett.*, **1997**, 509.

4 M. Hashimoto, S. Ujiie, and A. Mori, *Chem. Lett.*, **2000**, 758

5 A. Mori, K. Katahira, K. Kida, and H. Takeshita, *Chem. Lett.*, **1992**, 1767.

6 Y. Kurita, T. Nozoe, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **24**, 10 (1951); M. Kubo, T. Nozoe, and K. Kurita, *Nature*, **167**, 688 (1951).

7 D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, "Handbook of Liquid Crystals," VCH, Weinheim (1998).

8 H. Kawakuda and S. Yano, 14th Jpn. Symp. Liquid Crystals, Sendai, September, 1988, Abstr., No. 2D312; F. K. Beilstein, "Handbuch der Organischen Chemie," J. Springer, Berlin (1987).

9 H. Horino, T. Asao, and N. Inoue, *Bull. Chem. Soc. Jpn.*, **64**, 183 (1991).

10 Synthetic details and physical properties will be reported elsewhere. Elemental analyses. **1a**; Found: C, 70.99; H, 6.87%. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90%. **1b**; Found: C, 71.87; H, 7.33%. Calcd for $C_{28}H_{34}O_6$: C, 72.08; H, 7.35%. **1c**; Found: C, 72.65; H, 7.65%. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74%. **1d**; Found: C, 73.42; H, 8.05%. Calcd for $C_{32}H_{42}O_6$: C, 73.53; H, 8.10%. **1e**; Found: C, 74.12; H, 8.35%. Calcd for $C_{34}H_{46}O_6$: C, 74.15; H, 8.42%. **1f**; Found: C, 74.52; H, 8.67%. Calcd for $C_{36}H_{50}O_6$: C, 74.71; H, 8.71%. **1g**; Found: C, 75.11; H, 8.90%. Calcd for $C_{38}H_{54}O_6$: C, 75.21; H, 8.97%. **1h**; Found: C, 75.68; H, 9.22%. Calcd for $C_{40}H_{58}O_6$: C, 75.67; H, 9.21%. **1i**; Found: C, 75.92; H, 9.37%. Calcd for $C_{42}H_{62}O_6$: C, 76.09; H, 9.43%. **1j**; Found: C, 76.44; H, 9.65%. Calcd for $C_{44}H_{66}O_6$: C, 76.48; H, 9.63%. **1k**; Found: C, 76.68; H, 9.79%. Calcd for $C_{46}H_{70}O_6$: C, 76.84; H, 9.81%. **1l**; Found: C, 77.22; H, 10.10%. Calcd for $C_{50}H_{78}O_6$: C, 77.47; H, 10.14%. **3a**; Found: C, 75.98; H, 8.34%. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35%. **3b**; Found: C, 77.89; H, 9.65%. Calcd for $C_{34}H_{50}O_4$: C, 78.12; H, 9.64%.

11 Crystal data for **1c**: $C_{30}H_{38}O_6$, monoclinic, $P2_1/a$, $a = 13.770$ (1) Å, $b = 8.2007$ (6) Å, $c = 25.362$ (2) Å, $\beta = 103.688$ (3)°, $V = 2782.6$ (4) Å^3, $Z = 4$, $M_r = 494.63$, $D_x = 1.181$ Mgm^{-3}, refinement on F^2 (SHELXL97),[13] $wR(F^2) = 0.2820$. Crystal data for **2a**: $C_{24}H_{30}O_4$, triclinic, $P\bar{1}$, $a = 8.085$ (2) Å, $b = 24.996$ (5) Å, $c = 5.5008$ (9)Å, $\alpha = 93.80$ (1)°, $\beta = 107.634$ (5)°, $\gamma = 87.325$ (2)°, $V = 1056.6$ (3) Å^3, $Z = 2$, $M_r = 382.50$, $D_x = 1.202$ Mgm^{-3}, refinement on F^2 (SHELXL97),[13] $wR(F^2) = 0.2920$.

12 G. W. Gray and J. W. Goodby, "Smectic Liquids Crystals—Textures and Structures," Leonard Hill, Glasgow and London (1984).

13 G. M. Sheldrick, "SHELXL97. Program for the Refinement of Crystal Structures," University of Göttingen, Germany (1997).