Liquid Crystals with a 5-Cyanotropone Skeleton: 2-(4-Alkoxybenzoyloxy)-5-cyanotropones and 2-(4-Alkoxybenzoylamino)-5-cyanotropones

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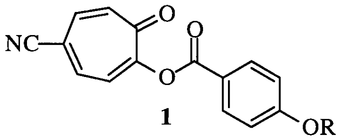
(Received March 9, 2000; CL-000234)

New troponoid liquid crystals with an electron-withdrawing cyano group at the C-5 position of tropolone and 2-aminotropone rings were prepared. Tropolone derivatives had nematic phases with lower thermal stabilities and smectic A phases with higher thermal stabilities than the corresponding benzenoids while thermal stabilities of the aminotropone derivatives were better than those of the benzenoids. The X-ray diffraction studies indicated that the ratios of the layer spacing measured in the smectic A phase and the calculated molecular length are 1.3 for a tropolone derivative and 1.45 for an aminotropone derivative. They formed interdigitated bilayers.

We have usually prepared troponoid liquid crystals with electron-donating substituents such as alkoxyl[1] and alkylamino[2] groups at the C-5 position of the tropolone ring. The presence of an electron-donating substituent at C-5 would enhance polarization of the tropone carbonyl group, which assisted to make intermolecular interaction strong. Among troponoid liquid crystals, we have observed that even monocyclic troponoids[3] exhibited mesogenic properties while the corresponding benzenoids were not mesogenic. In this paper, we report mesogenic properties of troponoid liquid crystals with an electron-withdrawing cyano group at C-5, which is one of the most useful substituents to stabilize mesogenic properties in benzenoid liquid crystals.[4] In the case of troponoids, however, introduction of an electron-withdrawing substituent at C-5 might be less favorable because both the tropone carbonyl group and the cyano group require electrons.



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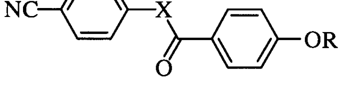
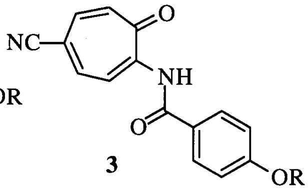


2 X = O **4** X = NH



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5-Cyanotropolone was prepared by the modified method of the known procedure.[5] Benzoylation of 5-cyanotropolone with 4-alkoxybenzoyl chlorides gave the corresponding 2-(4-alkoxybenzoyloxy)-5-cyanotropones (**1**) in reasonable yields.[6] The transition temperatures and the thermal behavior of the texture were determined using a polarizing microscope equipped with a hot stage as well as X-ray diffraction study. Compounds **1** had enantiotropic smectic A phases when the alkoxyl chain was long and they showed monotropic nematic phases when the alkoxyl chain was short. The smectic A phase was determined from observation of focal-conic fan and homeotropic textures. The nematic phase was assigned from observation of schlieren textures. The results are summarized in Table 1.

Troponoids **1** showed nematic phases with lower thermal stabilities than the corresponding benzenoids (**2**)[4] and smectic A phases with higher thermal stabilities than **2**. This is due to the presence of the carbonyl group, which played as a lateral dipole group.[7]

In order to elucidate molecular packing of the smectic A phase of **1**, we measured the X-ray diffraction pattern of **1f**. The smectic layer spacing (d) was observed to be ca. 40 Å. Since the calculated molecular length (l) by the AM 1 method is 30.4 Å, the layer spacing is 1.3 times as long as the molecular length. The d/l value is similar to the value (1.4)[8] of the benzenoids, where the cyano groups would come closely to cancel their dipole repulsion. From these evidences, we proposed a packing model of the smectic A phase of **1f** as shown in Figure 1, in which the core part including a cyano group had an antiparallel arrangement.

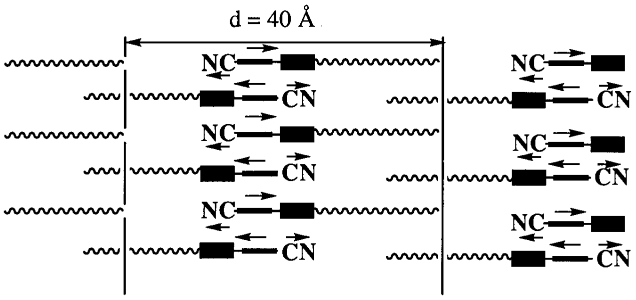

Figure 1 . Packing model of compound **1 f**.

On the other hand, we prepared 2-(4-alkoxybenzoylamino)-5-cyanotropones (**3**) from benzoylation of 2-amino-5-cyanotropone, which showed smectic A phases with higher transition temperatures than those of troponoid esters **1** and the corresponding benzenoid amides (**4**) as shown in Table 2. The X-ray diffraction study of **3e** indicated that d was 39.9 Å whereas l is calculated to be 27.5 Å. They also formed interdigitated bilayers (d/l=1.45).

Finally, when compared with the mesogenic properties between troponoid esters **1** and amides **3**, the latter was superior to the former. The X-ray crystallographic analyses indicated that the core part of a 2-(4-alkoxybenzoloxy)tropone derivative[9]

Table 1. Transition temperatures of troponoid esters **1** and benzenoid esters **2**[4]

	n	Transition temp / °C		n	Transition temp / °C
1a	5	Cr • 112.7 • (N • 57.2 •) Iso	**2a**	5	Cr • 87.0 • N • 96.0 • Iso
1b	6	Cr • 106.0 • (S_A • 54.2 • N • 57.1 •) Iso	**2b**	6	Cr • 70.5 • N • 81.0 • Iso
1c	8	Cr • 106.5 • (S_A • 80.5 • N • 84.7 •) Iso	**2c**	7	Cr • 71.6 • N • 82.0 • Iso
1d	9	Cr • 109.4 • (S_A • 95.3 •) Iso	**2d**	8	Cr • 75.6 • N • 88.0 • Iso
1e	12	Cr • 102.1 • S_A • 116.9 • Iso	**2e**	9	Cr • 62.0 • (S_A • 59.0 •) N • 84.0 • Iso
1f	14	Cr • 101.5 • S_A • 122.6 • Iso	**2f**	12	Cr • 73.0 • S_A • 89.5 • Iso

Cr: crystals, N: nematic phase, S_A: smectic A phase, Iso: isotropic liquid.

Table 2. Transition temperatures of troponoid amides **3** and benzenoid amides **4**

	n	Transition temp / °C		n	Transition temp / °C
3a	4	Cr • 185.0 • Iso	**4a**	6	Cr • 143.0 • Iso
3b	6	Cr • 157.5 • (S_A • 150.9 •) Iso	**4b**	8	Cr • 123.8 • Iso
3c	8	Cr • 166.4 • (S_A • 161.6 •) Iso	**4c**	10	Cr • 129.0 • Iso
3d	12	Cr • 152.4 • S_A • 169.2 • Iso	**4d**	12	Cr • 122.4 • (S_A • 107.5 •) Iso
3e	16	Cr • 145.1 • S_A • 166.3 • Iso	**4e**	16	Cr • 126.4 • (S_A • 123.7 •) Iso

was twisted by about 77° whereas the core part of a 2-(4-alkoxybenzoylamino)tropone derivative[10] was planar due to the intramolecular hydrogen bond between the tropone carbonyl group and the NH group. Therefore, amides **3** also would have a planar structure through an intramolecular hydrogen bond to increase thermal stabilities of mesophases more than melting point. The role of a cyano group would make it possible to have the arrangement by canceling dipole repulsion between a cyano group and a benzoyl group and between two tropone rings as shown in Figure 1.

In the case of benzenoids, however, amides **4** were inferior to esters **2**. This would be due to the intermolecular hydrogen bonding of amide groups, which increased the melting point to hide the mesogenic properties.

References and Notes

1 For example, M. Takemoto, A. Mori, and S. Ujiie, *Chem. Lett.*, **1999**, 1177.

2 A. Mori, R. Nimura, and H. Takeshita, *Chem. Lett.*, **1991**, 77.

3 A. Mori, M. Uchida, and H. Takeshita, *Chem. Lett.*, **1989**, 591; A. Mori, H. Takeshita, K. Kida, and M. Uchida, *J. Am. Chem. Soc.*, **112**, 8635 (1990); A. Mori, N. Kato, H. Takeshita, M. Uchida, H. Taya, and R. Nimura, *J. Mater. Chem.*, **1**, 799 (1991); K. Kida, A. Mori, and H. Takeshita, *Mol. Cryst. Liq. Cryst.*, **199**, 387 (1991).

4 V. V. Titov, E. I. Kovshev, A. I. Pavluchenko, V. T. Lazareva, and M. F. Grebenkin, *J. Phys. (Paris).*, Suppl. **36**, C1, 387 (1975); A. Göbl-Wunsch, G. Heppe, and R. Hopf, *Z. Naturforsch.*, **36a**, 213 (1981); N. H. Tinh, *Mol. Cryst. Liq. Cryst.*, **91**, 285 (1983); G. Heppke, and S. Pfeiffer, *Mol. Cryst. Liq. Cryst.*, **170**, 89 (1989); I. H. Ibrahim, H. Paulus, M. Mokhles, and W. Haase, *Mol. Cryst. Liq. Cryst.*, **A258**, 185 (1995); M. M. Naoum, H. Seliger, and E. Happ, *Liq. Cryst.*, **23**, 247 (1997).

5 J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, **1954**, 530.

6 Elemental analyses. **1a**: Found: C, 71.14; H, 5.71; N, 4.14%. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15%. **1b**: Found: C, 71.72; H, 6.04; N, 3.98%. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99%. **1c**: Found: C, 72.58; H, 6.65; N, 3.72%. Calcd for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69%. **1d**: Found: C, 73.20; H, 6.87; N, 3.56%. Calcd for $C_{24}H_{27}NO_4$: C, 73.26; H, 6.92; N, 3.56%. **1e**: Found: C, 74.21; H, 7.62; N, 3.28%. Calcd for $C_{27}H_{33}NO_4$: C, 74.45; H, 7.64; N, 3.22%. **1f**: Found: C, 74.92; H, 8.02; N, 3.08%. Calcd for $C_{29}H_{37}NO_4$: C, 75.13; H, 8.04; N, 3.02%. **3a**: Found: C, 70.68; H, 5.65; N, 8.77%. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69%. **3b**: Found: C, 71.96; H, 6.34; N, 8.03%. Calcd for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99%. **3c**: Found: C, 72.95; H, 6.91; N, 7.44%. Calcd for $C_{23}H_{26}N_2O_3$: C, 72.99; H, 6.92; N, 7.40%. **3d**: Found: C, 74.35; H, 7.88; N, 6.50%. Calcd for $C_{27}H_{34}N_2O_3$: C, 74.62; H, 7.89; N, 6.45%. **3e**: Found: C, 75.81; H, 8.59; N, 5.75%. Calcd for $C_{31}H_{42}N_2O_3$: C, 75.88; H, 8.63; N, 5.71%. **4a**: Found: C, 74.48; H, 6.89; N, 8.74%. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69%. **4b**: Found: C, 75.41; H, 7.49; N, 8.06%. Calcd for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99%. **4c**: Found: C, 76.13; H, 8.03; N, 7.43%. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.99; N, 7.40%. **4d**: Found: C, 76.76; H, 8.42; N, 7.03%. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.81; H, 8.43; N, 6.89%. **4e**: Found: C, 78.00; H, 9.18; N, 6.13%. Calcd for $C_{30}H_{42}N_2O_2$: C, 77.88; H, 9.15; N, 6.05%.

7 A. Mori, H. Taya, and H. Takeshita, *Chem. Lett.*, **1991**, 579.

8 P. E. Cladis, P. L. Finn, and J. W. Goodby, “Liquid Crystals and Ordered Fluids,” Gordon and Breach, New York (1982), Vol. 4, p. 203.

9 A. Mori, R. Nimura, M. Isobe, N. Kato, and H. Takeshita, in preparation.

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