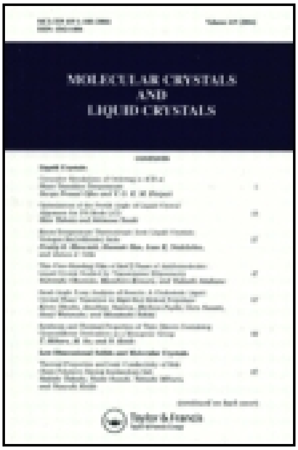

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Mesogenic Properties of 5-Cyanotropolone and 2-Amino-5-Cyanotropone Derivatives

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Mesogenic Properties of 5-Cyanotropolone and 2-Amino-5-Cyanotropone Derivatives

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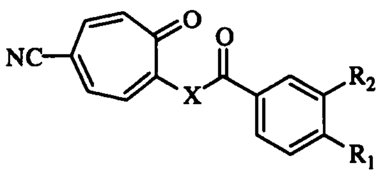
New 5-cyanotroponoid liquid crystals with a 3,4-dialkoxybenzoyloxy and a 3,4-dialkoxybenzoylamino substituent at the C-2 position were prepared. These derivatives exhibited interdigitated bilayer smectic A phases while the corresponding benzenoids were non-mesogenic. Thermal stabilities of these troponoids were lower than those of 2-(4-alkoxybenzoyloxy)-5-cyanotropones and 2-(4-alkoxybenzoylamino)-5-cyanotropones.

Keywords: 5-Cyanotroponoid liquid crystals; Forked mesogen; X-Ray diffraction study; Interdigitated bilayer smectic A phases

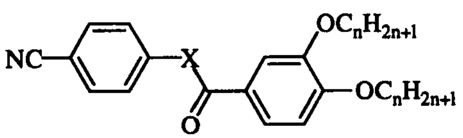
INTRODUCTION

Usually, cores of liquid crystals are consisted of six-membered rings. We are using a troponoid ring as the core because the carbonyl group of troponoids played important roles such as a lateral dipole group and an acceptor of hydrogen bondings to assist the exhibition of mesogenic properties. We introduced electron-donating substituents such as alkoxyl [1] and alkylamino [2] groups at the C-5 position of a tropolone ring, which would assist polarization of the tropone carbonyl group to make an intermolecular interaction strong.

We recently reported the mesogenic properties of troponoids liquid crystals (**1** and **2**) with an electron-withdrawing cyano group at the C-5 position and a 4-alkoxylbenzoyloxy and a 4-alkoxybenzoylamino group at the C-2 position of a tropone ring as well as the corresponding benzenoids [3]. Compared the thermal stability of their smectic A phases, troponoids had higher transition temperatures than the benzenoids. These results are parallel to those of the liquid crystals with an electron-donating substituent at the C-5 position of a tropolone ring. From X-ray diffraction studies, 5-cyanotroponoid derivatives formed interdigitated bilayer smectic A phases.



1 : X=O, R_1=OC_nH_{2n+1}, R_2=H
2 : X=NH, R_1=OC_nH_{2n+1}, R_2=H
3 : X=O, R_1 = R_2 = OC_nH_{2n+1}
4 : X=NH, R_1 = R_2 = OC_nH_{2n+1}



5 : X=O
6 : X=NH

In this paper, we report the thermal properties of 5-cyanotroponoids with a forked mesogen at the C-2 position. If 5-cyanotroponids with a forked mesogen at the C-2 position had bilayer molecular arrangements as observed in a 4-alkoxybenzoyloxy derivative [3], these compounds could behave as biforked mesogenic compounds, which would exhibit an interesting polymorphism in which both lamellar, columnar and cubic mesophases exist in the same series and in some cases in the same compounds [4].

RESULTS AND DISCUSSION

5-Cyanotroponoids were prepared by a modification of the known procedure [5]. Benzoylation of 5-cyanotropolone and 2-amino-5-cyanotropone gave the corresponding 2-(3,4-dialkoxybenzoyloxy)-5-cyanotropones (**3**) and 2-(3,4-dialkoxybenzoylamino)-5-cyanotropones (**4**) in reasonable yields.

TABLE 1. Transition temperatures of **1**

	n	Transition temp. / °C
1a	4	Cr • 116.4 • (N • 55.5 •) Iso
1b	6	Cr • 106.0 • (S_A • 54.2 • N • 57.1 •) Iso
1c	8	Cr • 106.5 • (S_A • 80.5 • N • 84.7 •) Iso
1d	10	Cr • 107.0 • (S_A • 105.7 •) Iso
1e	12	Cr • 102.1 • S_A • 116.9 • Iso
1f	14	Cr • 101.5 • S_A • 122.6 • Iso
1g	16	Cr • 102.4 • S_A • 125.5 • Iso

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 **3** and **4** had monotropic

TABLE 2. Transition temperatures of **2**

	n	Transition temp. / °C
2a	4	Cr • 185.0 • Iso
2b	6	Cr • 157.5 • (S_A • 150.9 •) Iso
2c	8	Cr • 166.4 • (S_A • 161.6 •) Iso
2d	10	Cr • 158.9 • S_A • 167.0 • Iso
2e	12	Cr • 152.4 • S_A • 169.2 • Iso
2f	14	Cr • 150.3 • S_A • 168.7 • Iso
2g	16	Cr • 145.1 • S_A • 166.3 • Iso

smectic A phases. The corresponding benzenoids **5** and **6** were, however, non-mesogenic. The results and the transition temperatures of compounds (**1**~**6**) are summarized in Tables 1~6.

5-Cyanotroponoids (**4**) with an amide substituent at C-2 showed monotropic smectic A phases with higher clearing points than those of the corresponding esters **3**. To explain the thermal stability of their smectic A phases of compounds **4**, we paid our attentions on an intramolecular hydrogen bond between the carbonyl group and the NH group, which made the molecule flat and rigid to enhance mesogenic properties. On the other hand, compared the thermal stability of their smectic A phases between forked type troponoids (**3**, **4**) and compounds (**1**, **2**), the former had lower transition temperatures than the latter.

In order to elucidate molecular packing of the smectic A phase of **3**, we measured the X-ray diffraction pattern of **3b**, which had monotropic smectic A phases. The smectic layer spacing was observed to be 1.4 times longer than the molecular length. From these evidences, we proposed a packing model of the smectic A phases of **3b**, in which the dipole moment of the troponoid cores faced oppositely to cancel each other and the alkyl chains of the benzoyl ring overlapped partly as observed in **1f** [3].

TABLE 3. Transition temperatures of **3**

	n	Transition temp. / °C
3a	8	Cr • 74.8 • (S_A • 72.8 •) Iso
3b	12	Cr • 85.1 • (S_A • 80.6 •) Iso

TABLE 4. Transition temperatures of **4**

	n	Transition temp. / °C
4a	8	Cr • 130.7 • (S_A • 118.5 •) Iso
4b	12	Cr • 129.4 • (S_A • 111.1 •) Iso

TABLE 5. Transition temperatures of **5**

	n	Transition temp. / °C
5a	8	Cr • 93.9 • Iso
5b	12	Cr • 98.3 • Iso

TABLE 6. Transition temperatures of **6**

	n	Transition temp. / °C
6a	8	Cr • 130.3 • Iso
6b	12	Cr • 125.9 • Iso

In the case of **3b**, however, core-core interaction of forked type troponoids with two alkoxy chains should be weaker than compounds (**1**) because **3b** has a wider terminal chain than **1**.

CONCLUSION

Forked type troponoids showed monotropic smectic A phases while the corresponding benzenoids were non-mesogenic. Thus, troponoid cores preferred to induce smectic phases. This is due to the presence of the carbonyl group, which played as a lateral dipole group. Although we observed that forked type troponoids formed an interdigitated bilayer structure, they showed only a monotropic smectic A phase. These results are, however, very unusual because it is quite rare that a forked compound with only two rings showed a smectic A phase.

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