Preparation of Sigmatropic 2-Acyloxy-5-perfluoroalkoxytropones: New Monocyclic Troponoid Liquid Crystals with an Enantiotropic Smectic A Phase

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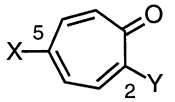
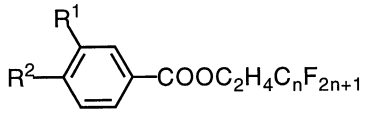
Monocyclic sigmatropic troponoid liquid crystals with a 2-(perfluoroalkyl)ethoxyl group at C-5 showed an enantiotropic smectic A phase. They have higher melting and clearing points than the corresponding non-fluorinated compounds, which exhibit a monotropic smectic A phase.

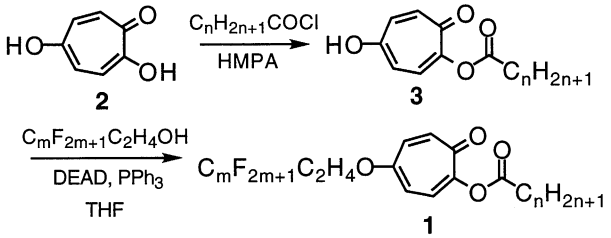
Previously we have reported that troponoids which have an acyl group at C-2 and an alkoxy group at C-5 showed a monotropic smectic A phase[1] whereas those having an alkoxy group at C-2 and an acyl group at C-5 did a virtual smectic A phase.[2] Similarly troponoids with acyl groups at C-2 and C-5 exhibited a monotropic smectic A phase.[3] Recently, Takenaka[4] has observed that monocyclic benzenoids having a fluorinated alkyl substituent were mesogenic, in which the fluorinated alkyl group worked as a core part. In this paper, we report the preparation of monocyclic troponoid liquid crystals **1** with a fluorinated alkyl group at C-5, which showed an enantiotropic smectic A phase.



X=OR, Y=OOCR': monotropic S_A
X = OOCR, Y=OR': virtual S_A
X=OOCR, Y=OOCR': monotropic S_A



Compounds **1** were prepared as follows; 5-hydroxytropolone (**2**) was treated with acyl chloride in the presence of HMPA to give 2-acyloxy-5-hydroxytropone (**3**), which was used for alkylation without purification. Alkylation of **3** with 2-(n-perfluoroalkyl)ethanol in the presence of DEAD and PPh_3 gave the desired **1** in 14-31% yields.[5] The ^1H NMR spectra of **1** revealed a [1,9] sigmatropic rearrangement, being similar to those of the corresponding non-fluorinated ones.[1]



Scheme 1.

The phase of **1** was determined by a differential scanning calorimeter (DSC) and the thermal behaviors of microscopic textures were observed using a polarizing microscope equipped with a hot stage. The transition temperatures and enthalpy changes are summarized in Table 1.

Compounds **1** showed an enantiotropic smectic A phase. The effect of the perfluoroalkyl group on melting and clearing points is shown in Figure 1, where the perfluoroalkyl group raised more clearing points than melting points.[6,7]

Table 2 summarizes the effects of the chain length at C-5 on the transition temperatures. The longer the length, the higher both melting and clearing points. While the chain length at C-2 was lengthened, melting and clearing points were lowered as shown in Table 1. This behavior was different to that of non-fluorinated series.[1]

Thus, a perfluoroalkyl group acted as a core to enhance the thermal stability of **1**, which enabled to prepare enantiotropic

Table 1. Transition temperatures (T/ °C) (left) and enthalpy changes (ΔH/ kJmol^{-1}) of **1**

	m	n	K		S_A		Iso	K		S_A		Iso
1a	6	7	•	84	•	100	•	•	24	•	6	•
1b	6	8	•	80	•	100	•	•	27	•	7	•
1c	6	9	•	80	•	97	•	•	26	•	6	•
1d	6	11	•	75	•	89	•	•	33	•	7	•
1e	8	7	•	101	•	123	•	•	36	•	7	•
1f	8	8	•	96	•	120	•	•	35	•	8	•
1g	8	9	•	99	•	118	•	•	40	•	8	•
1h	8	11	•	90	•	113	•	•	37	•	8	•
1i	10	9	•	109	•	134	•	•	37	•	9	•
1j	10	11	•	101	•	127	•	•	27	•	7	•
1k	10	13	•	94	•	122	•	•	34	•	7	•

K: Crystals, S_A: Smectic A phase, Iso: Isotropic liquid

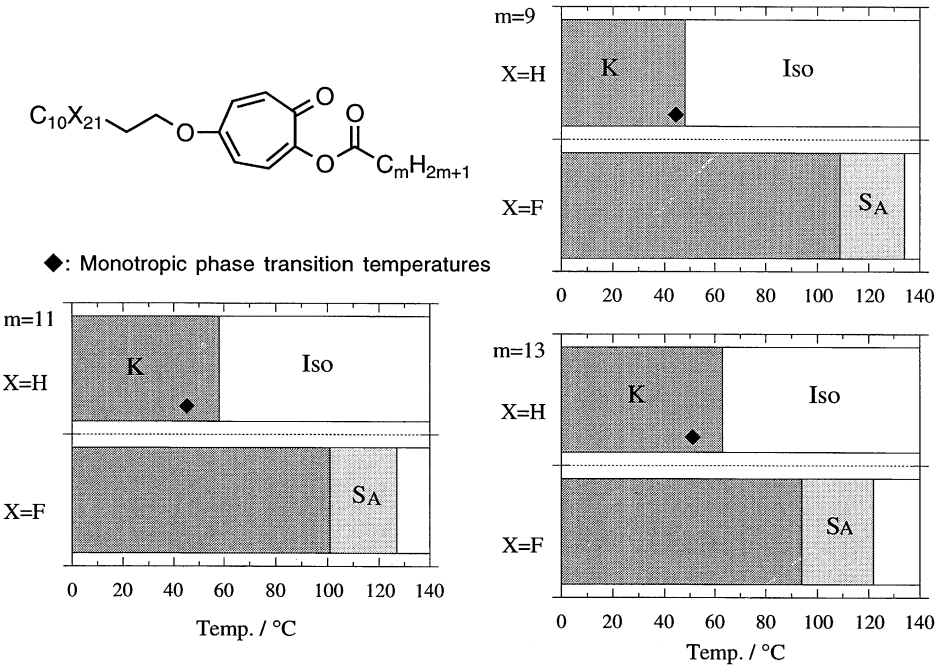


Figure 1. Comparison of the transition temperatures between compounds **1** and the corresponding non-fluorinated compounds.

Table 2. Effect of the chain length (m) on the transition temperatures (T/ °C)

	m	n	K		S_A		Iso
1c	6	9	•	80	•	97	•
1g	8	9	•	99	•	118	•
1i	10	9	•	109	•	134	•
1d	6	11	•	75	•	89	•
1h	8	11	•	90	•	113	•
1j	10	11	•	101	•	127	•

mesogenic compounds even though they are monocyclic. This is the first example that monocyclic troponoids show an enantiotropic mesogenic phase.

References and Notes

1 A. Mori, M. Uchida, and H. Takeshita, *Chem. Lett.*, **1989**, 591; A. Mori, H. Takeshita, K. Kida, and M. Uchida, *J. Am. Chem. Chem.*, **112**, 8635 (1990); K. Kida, A. Mori, and H. Takeshita, *Mol. Cryst. Liq. Cryst.*, **199**, 387 (1991).

2 A. Mori, S. Takematsu, M. Isobe, and H. Takeshita, *Chem. Lett.*, **1995**, 15.

3 A. Mori, R. Mori, and H. Takeshita, *Chem. Lett.*, **1991**, 1795.

4 S. Takenaka, *J. Chem. Soc., Chem. Commun.*, **1992**, 1748.

5 Physical data of **1**: **1a**; mp 84 °C; ^{1}H-NMR ($CDCl_3$) δ 0.88 (3H, t, *J*=7.5 Hz), 1.30-1.42 (8H, m), 1.76 (2H, m), 2.60 (2H, t, *J*=7.5 Hz), 2.67 (2H, m), 4.24 (2H, t, *J*=6.4 Hz), 6.70 (2H, br s), and 7.15 (2H, d, *J*=12.1 Hz); IR (KBr) ν 2963, 2862, 1758, 1586, 1537, 1390, 1245, 1210, 1185, 1141, 870, 700, and 651 cm^{-1}; MS m/z (%) 483 (100), 126 (25), 108 (31), 56 (63), and 42 (25); Found: C; 44.47, H; 2.97%. Calcd for $C_{23}H_{23}O_4F_{13}$: C; 45.26, H; 3.80%. **1b**; mp 80 °C; Found: C; 46.38, H; 4.10%. Calcd for $C_{24}H_{25}O_4F_{13}$: C; 46.16, H; 4.04%. **1c**; mp 80 °C; Found: C; 46.70, H; 4.32%. Calcd for $C_{25}H_{27}O_4F_{13}$: C; 47.03, H; 4.26%. **1d**; mp 75 °C; Found: C; 48.64, H; 4.76%. Calcd for $C_{27}H_{31}O_4F_{13}$: C; 48.66, H; 4.69%. **1e**; mp 101 °C; Found: C; 42.67, H; 3.11%. Calcd for $C_{25}H_{23}O_4F_{17}$: C; 42.27, H; 3.26%. **1f**; mp 96 °C; Found: C; 43.11, H; 3.23%. Calcd for $C_{26}H_{25}O_4F_{17}$: C; 43.11, H; 3.48%. **1g**; mp 99 °C; Found: C; 44.05, H; 3.76%. Calcd for $C_{27}H_{27}O_4F_{17}$: C; 43.91, H; 3.69%. **1h**; mp 90 °C; Found: C; 45.36, H; 4.11%. Calcd for $C_{29}H_{31}O_4F_{17}$: C; 45.44, H; 4.07%. **1i**; mp 109 °C; Found: C; 41.42, H; 3.37%. Calcd for $C_{29}H_{27}O_4F_{21}$: C; 41.54, H; 3.25%. **1j**; mp 101 °C; Found: C; 43.04, H; 3.17%. Calcd for $C_{31}H_{31}O_4F_{21}$: C; 42.97, H; 3.61%. **1k**; mp 94 °C; Found: C; 44.13, H; 3.81%. Calcd for $C_{33}H_{35}O_4F_{21}$: C; 44.31, H; 3.94%.

6 T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata, and H. Terauchi, *J. Mater. Chem.*, **1**, 169 (1991).

7 H. Bernhardt, W. Weissflog, and H. Mresse, *Chem. Lett.*, **1997**, 151.