JOURNAL OF
Materials
CHEMISTRY

Preparation of troponoid liquid crystals with a flexible oxymethylene linking unit

Akira Mori,*[a] **Hisashi Taya,**[b] **Hitoshi Takeshita**[c] **and Seiji Ujiie**[d]

[a]*Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816, Japan*
[b]*Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816, Japan*
[c]*Tohwa Institute for Oriental Science, Tohwa University, Chikushi-ga-oka, Minami-ku, Fukuoka 815, Japan*
[d]*Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Matue 690, Japan*

2-Benzyloxytropones, which have a saturated oxymethylene ($-CH_2O-$) linking unit, show a monotropic smectic A phase while the corresponding alkoxybenzyl alkoxyphenyl ethers have poor mesogenic properties. The tropone carbonyl group acting as a dipolar lateral substituent enhances the smectic thermal stability.

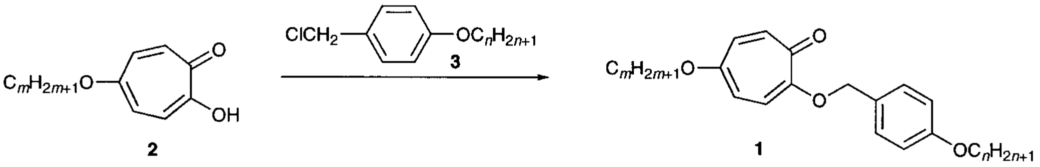
A typical liquid crystal structure generally consists of a rigid core part and two terminal chains. The core usually has aromatic rings connected either directly or through a linking unit. It has been recognized that flexible, saturated linking units such as $-CH_2O-$, $-CH_2CH_2-$ and $-OCH_2CH_2O-$ are less favorable for the appearance of a mesophase[1] since these linking units do not preserve the linearity of the molecules. In this paper, we describe the synthesis and mesomorphic properties of 2-benzyloxytropone derivatives, which showed the monotropic smectic A (S_A) phase when the alkoxy groups were lengthened.

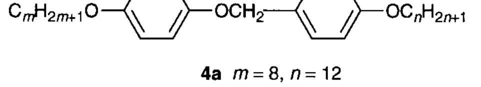
The ^1H NMR spectra of 5-alkoxy-2-(4-alkoxybenzyloxy)tropones **1** showed no broadened signals at room temperature, eliminating the occurrence of [1,9] sigmatropy as observed in 2-acyloxytropone derivatives.[3–6] The phase transition temperatures were determined by differential scanning calorimetry (DSC) and the thermal behavior of the microscopic texture was observed using a polarizing microscope equipped with a hot stage. The results are summarized in Table 1.

All mesogenic compounds **1** showed a monotropic S_A phase. This contrasts with that of corresponding benzenoid compounds with a flexible, saturated linking unit, which are known to be nonmesogenic or mesogenic with low thermal persistence.[1] The benzene derivative **4b** exhibited no mesophase, but compound **4a** showed a mosaic texture and homeotropic structure. The X-ray diffraction pattern of **4a** at 76 °C showed two sharp reflections at 36.7 and 2.83 Å, which suggested the exhibition of a smectic B (S_B) phase.

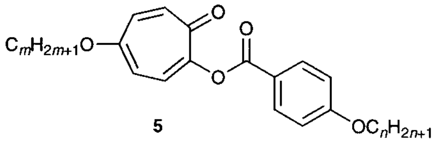
Table 2 summarizes the comparison with transition temperatures between **1** and the corresponding benzoyloxy series **5**.[3,6] Compound **5** with a $-COO-$ linking unit had a lower melting point and a higher clearing point than **1**. This parallels the behavior of the benzenoid compounds as shown in Table 3.[7–10] Although the formation of liquid crystals from **1** is less likely than from **5**, **1** is more favorable than benzenoids **4**.

Table 4 summarizes the transition temperatures of **1** when the alkyl length of the tropone ring was changed and that of the benzyloxy group was fixed. The length of the alkyl group of the tropone ring affected the clearing point more than the melting point whereas the alkyl chain length on the benzyloxy group did not affect the clearing point so much. On the other hand, when the alkyl length of the benzyloxy group was changed, the melting point changed more than the clearing point, as shown in Table 1. Further, compounds **1-Cl** and

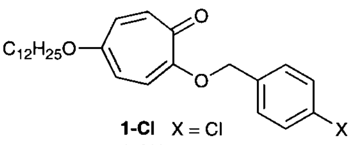




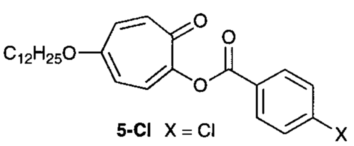
4a $m=8$, $n=12$
4b $m=n=12$



5



1-Cl X = Cl
1-CN X = CN



5-Cl X = Cl
5-CN X = CN

Table 1 Transition temperatures (T/°C) and, in parentheses, enthalpy changes (ΔH/kJ mol^{-1}) of **1**

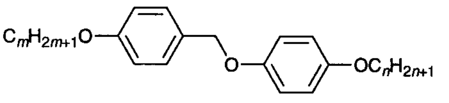
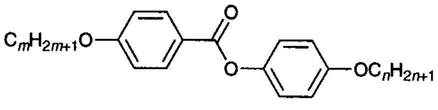
	m	n	K		S_A		I		m	n	K		S_A		I
a	4	12	·	90 (50.4)	·	58	·	**m**	11	1	·	68			·
b	6	6	·	88			·	**n**	11	6	·	91			·
c	6	7	·	85 (45.6)	·	64 (8.5)	·	**o**	11	7	·	86 (45.7)	·	79	·
d	6	8	·	83 (40.0)	·	65 (15.9)	·	**p**	11	8	·	86 (45.7)	·	80 (17.2)	·
e	6	10	·	84 (46.8)	·	67 (8.8)	·	**q**	11	10	·	71 (51.0)	·	62	·
f	6	12	·	86 (47.5)	·	70 (9.0)	·	**r**	11	12	·	81 (53.2)	·	77 (13.7)	·
g	8	4	·	94			·	**s**	12	1	·	70			·
h	8	6	·	87 (38.8)	·	70	·	**t**	12	4	·	91			·
i	8	7	·	88 (47.6)	·	74 (9.2)	·	**u**	12	6	·	71			·
j	8	8	·	82 (42.7)	·	74 (9.1)	·	**v**	12	7	·	89 (48.5)	·	77	·
k	8	10	·	80 (46.3)	·	75 (11.9)	·	**w**	12	8	·	83 (35.7)	·	80	·
l	8	12	·	81 (50.1)	·	75 (11.9)	·	**x**	12	10	·	87 (48.9)	·	81 (12.9)	·
								y	12	12	·	83 (44.7)	·	80 (14.2)	·

Table 2 Comparison of transition temperatures (T/°C) between **1** and **5**

	1					**5**							
(m, n)	K		S_A		I	K	S_C		S_A		N		I
(6, 12)	·	86	·	70	·	·	(· 54)[b]			58	·	66	·
(8, 12)	·	81	·	75	·	·		67	·			76	·
(11, 12)	·	81	·	77	·	·		51	·			85	·
(12, 4)	·	91			·	·	(· 63)[b]	64	·			70	·
(12, 12)[a]	·	83	·	80	·	·		64	·			90	·

[a]Recrystallization temperature was 55 °C. [b]The value in parentheses is the monotropic transition temperature.

Table 3 Comparison of the transition temperatures (T/°C) of ethers and esters

(m, n)		
(1, 5)	K 93 (N 38) I[a]	K 67 N 72.5 I[d]
(5, 6)	K 89 I[b]	K 57.5 N 84.5 I[d]
(12, 8)	K 91 (S_B 76) I[c]	K 70 (S 57.5) S_C 86 S_A 90.5 I[e]

[a]Ref. 7. [b]Ref. 9. [c]This work. [d]Ref. 8. [e]Ref. 10.

1-CN with a chlorine atom and a cyano group were not mesogenic although the corresponding troponoid **5-CN** showed monotropic smectic A phases.[6]

From the contrasting results of the troponoid and the benzenoid derivatives, mesophases can presumably be stabilized by the tropone carbonyl group, whose permanent dipole moment increases the attractive dispersion force between molecules.[11,12] The carbonyl group of tropones plays a crucial role as a polar lateral substituent in the formation of the mesophase.

Experimental

Elemental analyses were performed at Kyushu University. The NMR spectra were measured using GSX 270H spectrometers in $CDCl_3$, unless otherwise specified, and the chemical shifts are expressed in δ units, with J values in Hz. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds using a JASCO IR-A 102 spectrometer. The UV spectra were

Table 4 Effect on the transition temperatures (T°C) and, in parentheses, enthalpy changes (ΔH/kJ mol^{-1}) of **1** when the alkyl chain length (m) was changed

	m	n	K		S_A		I		m	n	K		S_A		I
b	6	6	·	88			·	**e**	6	10	·	84 (46.8)	·	67 (8.8)	·
h	8	6	·	87 (38.8)	·	70	·	**k**	8	10	·	80 (46.3)	·	75 (11.9)	·
n	11	6	·	91			·	**q**	11	10	·	71 (51.0)	·	62	·
u	12	6	·	71			·	**x**	12	10	·	87 (48.9)	·	81 (12.9)	·
c	6	7	·	85 (45.6)	·	64 (8.5)	·	**f**	6	12	·	86 (47.5)	·	70 (9.0)	·
i	8	7	·	88 (47.6)	·	74 (9.2)	·	**l**	8	12	·	81 (50.1)	·	75 (11.9)	·
o	11	7	·	86 (45.7)	·	79	·	**r**	11	12	·	81 (53.2)	·	77 (13.7)	·
v	12	7	·	89 (48.5)	·	77	·	**y**	12	12	·	83 (44.7)	·	80 (14.2)	·
d	6	8	·	83 (40.0)	·	65 (15.9)	·								
j	8	8	·	82 (42.7)	·	74 (9.1)	·								
p	11	8	·	86 (45.7)	·	80 (17.2)	·								
w	12	8	·	83 (35.7)	·	80	·								

measured using Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.†

Preparation of 1

When the sodium salts of 5-alkoxytropolones **2**,[2] prepared with NaH in hexamethylphosphoric triamide (HMPT) at room temp., were reacted with 4-alkoxybenzyl chloride **3** overnight at 50 °C, compounds **1** were obtained in 42–65% yields after SiO_2 chromatography.

1a: mp 90 °C; δ_H 0.88 (3H, t, J 6.6), 0.96 (3H, t, J 7.3), 1.26–1.53 (20H, m), 1.69–1.82 (4H, m), 3.84 (2H, t, J 6.6), 3.93 (2H, t, J 6.6), 5.13 (2H, s), 6.21 (1H, dd, J 11.0, 2.6), 6.80 (1H, d, J 11.0), 6.87 (2H, d, J 8.8), 7.05 (1H, dd, J 13.2, 2.6), 7.20 (1H, d, J 13.2), and 7.32 (2H, d, J 8.8). δ_C 13.8, 14.1, 19.2, 22.7, 26.1, 29.3, 29.4 (2C), 29.6 (4C), 31.0, 31.9, 68.1, 68.2, 70.9, 107.9, 114.6 (2C), 118.3, 128.1, 129.0 (2C), 132.9, 138.0, 158.7, 159.0, 159.5, and 179.9. ν/cm^{-1} 2925, 2850, 1560, 1510, 1450 and 1250. m/z (%): 468 (M^+, 7), 276 (21), 275 (100), and 107 (14). Calc. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%. Found: C, 76.88; H, 9.51%.

1b: mp 88 °C; Calc. for $C_{26}H_{36}O_4$: C, 75.69; H, 8.80%. Found: C, 75.82; H, 8.75%.

1c: mp 85 °C; Calc. for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98%. Found: C, 76.30; H, 9.03%.

1d: mp 83 °C; Calc. for $C_{28}H_{40}O_4$: C, 76.32; H, 9.15%. Found: C, 76.49; H, 9.24%.

1e: mp 84 °C; Calc. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%. Found: C, 77.08; H, 9.44%.

1f: mp 86 °C; Calc. for $C_{32}H_{48}O_4$: C, 77.38; H, 9.74%. Found: C, 77.34; H, 9.54%.

1g: mp 94 °C; Calc. for $C_{29}H_{36}O_4$: C, 75.70; H, 8.80%. Found: C, 76.00; H, 8.81%.

1h: mp 87 °C; Calc. for $C_{28}H_{40}O_4$: C, 76.32; H, 9.15%. Found: C, 76.15; H, 9.08%.

1i: mp 88 °C; Calc. for $C_{29}H_{42}O_4$: C, 76.60; H, 9.30%. Found: C, 76.51; H, 9.21%.

1j: mp 82 °C; Calc. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%. Found: C, 77.00; H, 9.40%.

1k: mp 80 °C; Calc. for $C_{32}H_{48}O_4$: C, 77.37; H, 9.74%. Found: C, 77.22; H, 9.60%.

1l: mp 81 °C; Calc. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99%. Found: C, 77.87; H, 10.04%.

1m: mp 68 °C; Calc. for $C_{26}H_{36}O_4$: C, 75.69; H, 8.79%. Found: C, 76.05; H, 8.75%.

1n: mp 91 °C; Calc. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61%. Found: C, 77.28; H, 9.54%.

1o: mp 86 °C; Calc. for $C_{32}H_{48}O_4$: C, 77.38; H, 9.74%. Found: C, 77.42; H, 9.59%.

1p: mp 86 °C; Calc. for $C_{33}H_{50}O_4$: C, 77.60; H, 9.87%. Found: C, 77.67; H, 9.57%.

1q: mp 71 °C; Calc. for $C_{35}H_{54}O_4$: C, 78.02; H, 10.10%. Found: C, 77.70; H, 10.11%.

1r: mp 81 °C; Calc. for $C_{37}H_{58}O_4$: C, 78.40; H, 10.31%. Found: C, 78.88; H, 10.18%.

1s: mp 70 °C; Calc. for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98%. Found: C, 75.94; H, 8.80%.

1t: mp 91 °C; Calc. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%. Found: C, 76.67; H, 9.45%.

1u: mp 71 °C; Calc. for $C_{32}H_{48}O_4$: C, 77.38; H, 9.74%. Found: C, 77.23; H, 9.53%.

1v: mp 89 °C; Calc. for $C_{33}H_{50}O_4$: C, 77.60; H, 9.87%. Found: C, 77.54; H, 9.72%.

1w: mp 83 °C; Calc. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99%. Found: C, 78.06; H, 9.87%.

1x: mp 87 °C; Calc. for $C_{36}H_{56}O_4$: C, 78.21; H, 10.21%. Found: C, 78.39; H, 10.14%.

1y: mp 72 °C; Calc. for $C_{38}H_{60}O_4$: C, 78.57; H, 10.41%. Found: C, 78.75; H, 10.21%.

1-Cl: mp 73 °C; Calc. for $C_{38}H_{59}O_4Cl$: C, 74.17; H, 9.66%. Found: C, 73.80; H, 9.49%.

1-CN: mp 102 °C; Calc. for $C_{27}H_{35}O_3N$: C, 76.92; H, 8.37; N, 3.32%. Found: C, 77.12; H, 8.42; N, 3.54%.

Preparation of 4

Similarly compounds **4** were prepared from 4-alkoxyphenols and 4-alkoxybenzyl chlorides. **4a**: mp 91 °C; δ_H 0.86–0.90 (6H, m), 1.26–1.46 (28H, m), 1,70–1.82 (4H, m), 3.89 (2H, t, J 6.6), 3.95 (2H, t, J 6.6), 4.92 (2H, s), 6.81 (2H, d, J 9.5), 6.86 (2H, d, J 9.5), 6.89 (2H, d, J 8.8), and 7.32 (2H, d, J 8.8). δ_C 14.1, 22.7 (2C), 26.1 (2C), 29.3 (2C), 29.4 (2C), 29.6 (4C), 29.7 (2C), 31.8, 31.9, 68.1, 68.6, 70.6, 114.6 (2C), 115.4 (2C), 115.8 (2C), 129.1, 129.2 (2C), 152.9, 153.5, and 159.0. ν/cm^{-1} 2925, 2850, 1510, 1235 and 1020. Calc. for $C_{33}H_{52}O_3$: C, 79.79; H, 10.55%. Found: C, 79.73; H, 10.30%.

4b: mp 97 °C; Calc. for $C_{37}H_{60}O_3$: C, 80.38; H, 10.94%. Found: C, 80.21; H, 10.76%.

References

1 G. W. Gray, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, London, New York, San Francisco, 1979, ch. 1.
2 A. Mori, H. Taya and H. Takeshita, *Chem. Lett.*, 1991, 579.
3 A. Mori, M. Uchida and H. Takeshita, *Chem. Lett.*, 1989, 591.
4 A. Mori, H. Takeshita, K. Kida and M. Uchida, *J. Am. Chem. Soc.*, 1990, **112**, 8635.
5 K. Kida, A. Mori and H. Takeshita, *Mol. Cryst. Liq. Cryst.*, 1991, **199**, 387.
6 A. Mori, N. Kato, H. Takeshita, M. Uchida, H. Taya and R. Nimura, *J. Mater. Chem.*, 1991, **1**, 799.
7 The transition temperature to the N phase was determined by extrapolation. See N. Carr and G.W. Gray, *Mol. Cryst. Liq. Cryst.*, 1985, **124**, 27.
8 D. Demus, H.-J. Deutschen, D. Marzotko, H. Kresse and A. Wiegleben, in *Proceedings of International Liquid Crystal Conference*, Bangalore, 1980, p. 97.
9 T. Kitamura, H. Yokokura, A. Mukoh and M. Sato, in *Abstracts of 6th Symposium of Liquid Crsytals*, Sendai, 1980, IR08.
10 D. Demus, H. Demus and H. Zaschke, *Flüssige Kristalle in Tabellen Deutscher Verlag für Grundstoffindustrie*, Leipzig, 1976.
11 K. Takatoh, K. Sunohara and M. Sakamoto, *Mol. Cryst. Liq. Cryst.*, 1988, **164**, 167.
12 R. Brettle, D. A. Dunmur, L. D. Farrand, N. J. Hindley and C. M. Marson, *Chem. Lett.*, 1993, 1663.

Paper 7/04536K; *Received* 27th *June*, 1997

---

† Further data are available as supplementary material (SUP 57321; 12 pp.) deposited with the British Library. Details are available from the editorial office.