

Synthesis and Thermal Properties of Liquid Crystals having a Carbonyl Group at the Terminal Position

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This paper describes synthesis and thermal properties of liquid crystals (LCs) with a carbonyl group, such as 1,3-dioxane-2-one, pyran-2-one, benzo[1,3]oxathiol-2-one, or 3*H*-benzofuran-2-one at the terminal position. These compounds with a short alkoxy (alkyl) chain are non-mesogenic, while those with a medium and/or long alkoxy one show a nematic and/or smectic A phase(s). Dielectric properties for these compounds are also examined in a mixed state. The results indicate that these compounds are suitable composites for enhancing a positive dielectric anisotropy in non-polar and/or polar nematic LC(s).

Key words: Polar liquid crystals, Synthesis, Nematic phase, Smectic A phase, Dielectric properties

1. INTRODUCTION

Dielectric properties are one of the important physical parameters of liquid crystal (LC) materials for display device. The dielectric properties are frequently correlated with the dipole moment arising from polar functional groups within the molecule. Therefore, a lot of liquid crystals having a polar group such as a cyano group or a nitro one have been extensively developed.¹

It has been well known that carbonyl groups such as lactone and cyclic carbonate also have a large dipole moment being comparable with cyano and nitro ones.²⁻⁴ Thus, we are interested in the effectiveness of a pyran-2-one, benzo[1,3]oxathiol-2-one, and 3*H*-benzofuran-2-one skeletons as a composite of liquid crystal molecules.

This paper describes the synthesis and thermal properties of 5-(4-*n*-alkoxyphenyl)-1,3-dioxane-2-ones (1), 5-(4-*n*-alkoxyphenoxycarbonyl)-pyrane-2-ones (2), 5-(4-*n*-alkoxybenzoyloxy)- (3), 5-(*trans*-4-*n*-alkylcyclohexylcarbonyloxy)- (3') benzo[1,3]oxathiol-2-ones, 5-(4-*n*-alkoxybenzoyloxy)- (4), and 5-(4-*n*-pentylbenzoyloxy)- (4') 3*H*-benzofuran-2-ones as shown in Fig. 1. Dielectric properties for these compounds are also examined and the results are discussed in terms of the molecular structures.

2. EXPERIMENTAL

Materials: Compounds 1 were prepared according to ref. 2. Compounds 2-4 were synthesized by an esterification of the corresponding phenols, such as 4-alkoxyphenol (2), 6-hydroxy-1,3-benzoxathiol-2-one (3, 3'), 2,5-dihydroxy phenylacetic γ -lactone (4, 4'), and carboxylic acids, i.e. coumalic acid (2), 4-*n*-alkoxybenzoic acid (3, 4), *trans*-4-*n*-alkylcyclohexanecarboxylic acid (3'), and 4-*n*-pentylbenzoic acid (4') with a DCC method. Chemical structures and purity for

compounds 1-4' were confirmed by HPLC, ¹H NMR (JEOL EX-270), where CDCl₃ was used as a solvent, and IR (Horiba FT-200) spectroscopies.

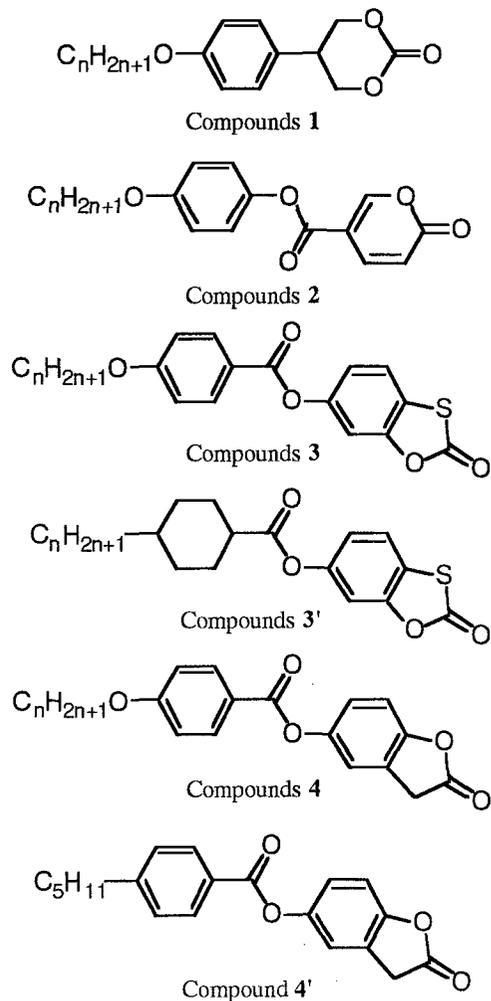


Fig. 1 Chemical structures for compounds 1-4'

A typical procedure for synthesis of pentyloxy homologue of **2** is as follows.

A mixture of 4-*n*-pentyloxyphenol (1.0 g, 5.5 mmol) and coumalic acid (0.78 g, 5.6 mmol), DCC (1.2 g, 5.8 mmol), and a catalytic amount of *N,N*-dimethylaminopyridine in 20 ml of dry THF was allowed to stir overnight at room temperature. After dilution with toluene, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue remaining after evaporation was chromatographed on silica gel, where chloroform was used as an eluent. Recrystallization from toluene and ethanol yields 1.1 g (65%).

¹H NMR; δ =0.91 (3H, t, J =6.6 Hz), 1.25–1.50 (4H, m), 1.79 (2H, qui., J =7.0 Hz), 3.95 (2H, t, J =6.6 Hz), 6.40 (1H, d, J =9.9 Hz), 6.92 (2H, d, J =9.2 Hz), 7.06 (2H, d, J =9.2 Hz), 7.89 (1H, dd, J =9.9, 2.6 Hz), 8.50 (1H, d, J =2.6 Hz) ppm.

IR (KBr disc); ν =1735 and 1760 cm^{-1}

The other compounds were synthesized by a similar procedure using the corresponding carboxylic acids and phenols.

Methods: Mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system FP900.

Transition temperatures were determined using a Seiko SSC-5200 differential scanning calorimeter (DSC), where indium (99.9 %) was used as a calibration standard (mp 156.6 °C, 28.4 J g⁻¹). Dielectric anisotropy ($\Delta\epsilon$) was measured in a mixed state where 5–15 mol% of **1–4'** were mixed with host LC materials; non-polar nematic LC (Mixture I*) and/or polar one (Mixture II**), as noted in Footnotes. Molecular structures for **1–4'** were estimated by MOPAC AM1 method.

3. RESULTS AND DISCUSSION

Thermal properties: Transition temperatures for compounds **1–4'** are summarized in Table I, and those for **2**, **3**, and **4** are plotted against the carbon number (*n*) as shown in Fig. 2. Compounds **1** and **2** show a smectic A (SmA) phase in a rapid cooling process from pentyloxy and heptyloxy homologues, respectively, where the SmA–isotropic (I) phase transition temperatures are increased on ascending the homologues. Compounds **3** also show a monotropic SmA phase from undecyloxy homologue, where the SmA–I transition temperature is 61 °C. Compounds **3'**, which have a cyclohexyl group in stead of phenyl one in **3**, do not show any mesomorphic property in a rapid cooling process, due to a high melting point. Interestingly, compounds **4** show a nematic (N) phase in a rapid cooling process from an earlier member. The N–I transition temperatures are increased on ascending the homologues with an even-odd alternation as shown in Fig 2(c). The octyloxy homologue shows a monotropic SmA phase in addition to the N phase. The transition temperatures for the SmA–I are also increased on ascending the homologue, resulting an enantiotropic SmA phase from the nonyloxy homologue. Compound **4'**, which has an alkyl group in stead of alkoxy one in

4, does not show any mesomorphic property, nevertheless **4'** has a lower melting point than **4**.

Table I, Transition temperatures and latent heats for compounds **1–4'**.

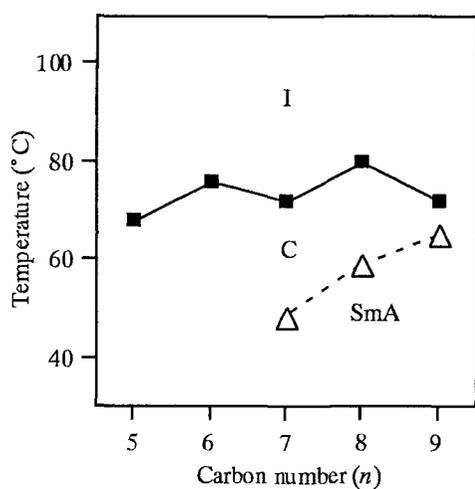
| | <i>n</i> | Transition temperature/°C [Latent heat/kJ mol ⁻¹] | | | | |
|----------|-----------|--|----------------|--------------|---|---|
| | | C | SmA | N | I | |
| 1 | 4 | • 86 [27.3] | – | – | • | |
| | 5 | • 60 [30.2] | (• 12) | – | • | |
| | 6 | • 61 [23.7] | (• 39) | – | • | |
| 2 | 5 | • 68 | – | – | • | |
| | 6 | • 76 | – | – | • | |
| | 7 | • 72 [20.4] | (• 48) | – | • | |
| | 8 | • 80 | (• 59) | – | • | |
| | 9 | • 72 [20.4] | (• 65) | – | • | |
| | 3 | 5 | • 84 | – | – | • |
| 8 | | • 101 | – | – | • | |
| 10 | | • 84 | – | – | • | |
| | 11 | • 95 [55.2] | (• 61) | – | • | |
| | 12 | • 105 [34.3] | (• 65) | – | • | |
| | 3' | 3 | • 122 | – | – | • |
| 4 | | • 110 | – | – | • | |
| 5 | | • 121 | – | – | • | |
| 4 | 5 | • 80 [28.5] | – | (• 35) *1 | • | |
| | 6 | • 64 [31.3] | – | (• 47) | • | |
| | 7 | • 75 [29.7] | – | (• 51) | • | |
| | 8 | • 75 [22.1] | (• 56) | (• 62) | • | |
| | 9 | • 56 [21.7] | • 70 | – | • | |
| | 10 | • 58 [23.5] | • 80 | – | • | |
| | 11 | • 60 [25.9] | • 84 | – | • | |
| | 4' | 5 | • 68 [20.6] | – | – | • |

C, SmA, N, and I indicate crystal, smectic A, nematic, and isotropic phases, respectively.

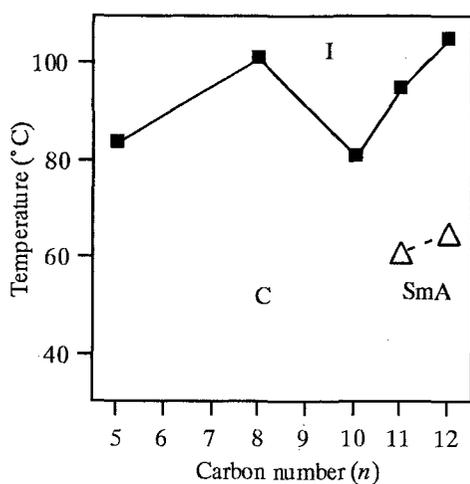
Parentheses indicate a monotropic transition.

Brackets indicate a latent heat.

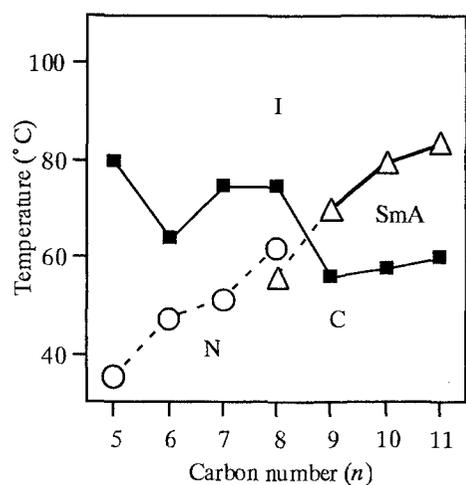
*1 The latent heat could not be observed by a DSC thermogram. *2 Total of the SmA–N and N–I transitions.



(a)



(b)



(c)

Fig. 2. Plots of transition temperature vs. carbon number, n , for (a) 2, (b) 3, and (c) 4: (○) N-I, (△) SmA-I, (■) melting point; the N-I and SmA-N transitions below the melting point are a monotropic process.

Dielectric properties: In order to determine the effects of the terminal carbonyl groups on dielectric and mesomorphic properties, dielectric anisotropy and mesomorphic properties, dielectric anisotropy in mixed states and the thermal properties were investigated. Table II and III show the results in non-polar Mixture I* and polar mixture II**, respectively.

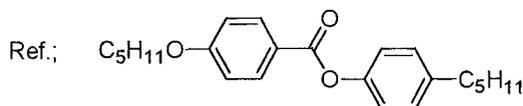
Table II, Dielectric anisotropy and N-I transition temperature for compounds 1-4' on in Mixture I* (see footnotes)

| Compounds | wt% | N-I/°C (N-I _{ex}) | $\Delta\epsilon^{25}$ ($\Delta\epsilon_{ex}^{25}$) |
|-----------|-----|--------------------------------|---|
| none | | 75 | -1.4 |
| 1 (n=4) | 5 | 66 | -0.3 |
| | | (-101) | (21.4) |
| | 10 | 59 | 0.3 |
| | | (-83) | (15.2) |
| 2 (n=5) | 15 | 63 | 0.0 |
| | | (-2) | (8.3) |
| | 15 | 65 | -0.0 |
| | | (7) | (8.1) |
| 3 (n=5) | 10 | 71 | 0.1 |
| | | (34) | (13.5) |
| 3' (n=5) | 5 | 72 | -1.2 |
| | | (29) | (2.6) |
| 4 (n=5) | 15 | 69 | 0.2 |
| | | (37) | (9.7) |
| 4' (n=5) | 15 | 65 | 0.2 |
| | | (10) | (9.2) |

$\Delta\epsilon_{ex}^{25}$ and N-I_{ex} are $\Delta\epsilon$ at 25 °C and extrapolated N-I transition temperatures, respectively.

Table III, Dielectric anisotropy and N-I transition temperature for compound 1-3 in Mixture II** (see footnotes)

| Compounds | wt% | N-I/°C (N-I _{ex}) | $\Delta\epsilon^{25}$ ($\Delta\epsilon_{ex}^{25}$) |
|-----------|-----|--------------------------------|---|
| none | | 72 | 11.0 |
| 1 (n=4) | 3 | 69 | 11.6 |
| | | (-35) | (8.4) |
| | 15 | 55 | 10.5 |
| | | (-43) | (4.3) |
| 2 (n=5) | 10 | | 10.8 |
| | | | (3.6) |
| | 15 | | 10.4 |
| | | | (3.6) |
| 3 (n=5) | 10 | 65 | 12.1 |
| | | (9) | (16.6) |
| Ref. | 15 | (49) | (4.9) |



The extrapolated N-I (N-I_{ex}) transition temperatures for butoxy and pentyloxy homologues of 1 in Mixture I are estimated to be -101 and -83 °C, respectively, as shown in Table II. On the other hand, those in Mixture II are -35 ($n=4$) and -43 ($n=5$) °C as shown in Table III. The N-I_{ex} transition temperatures for pentyl and

heptyl homologues of **2** in Mixture I are -2 and 7 °C, respectively. The $N-I_{ex}$ transition temperature for **3** in Mixture I is 34 °C, which is higher than that in Mixture II (9 °C), as a result. The $N-I_{ex}$ transition temperature for **3'**, **4**, and **4'** are 29, 37, and 10 °C, respectively.

As can be seen from Table II, all compounds show a positive dielectric anisotropy ($\Delta\epsilon > 0$) in Mixture I, where the values of an extrapolated $\Delta\epsilon$ at 25 °C are estimated to be 21.4 for butoxy and 15.2 for pentyloxy homologues of **1**, 8.3 for pentyloxy and 8.1 for heptyloxy homologues of **2**, 13.5 for pentyloxy homologue of **3**, 2.6 for **3'**, 9.7 for pentyloxy homologue of **4** and 9.2 for **4'**.

The effective order for enhancing $\Delta\epsilon$ in Mixture I is expressed as follows:



In the case of Mixture II, furthermore, the extrapolated $\Delta\epsilon$ are estimated to be 8.4 for butoxy and 4.3 for pentyloxy homologues of **1**, 3.6 for pentyloxy and heptyloxy homologues of **2**, and 16.6 for pentyloxy homologue of **3**. The effective order for enhancing $\Delta\epsilon$ in Mixture II is consequently expressed as follows:



Fig. 3 shows molecular geometries of the terminal substituents for **1-4'** and angles of the carbonyl group with the longitudinal axis of the molecules.

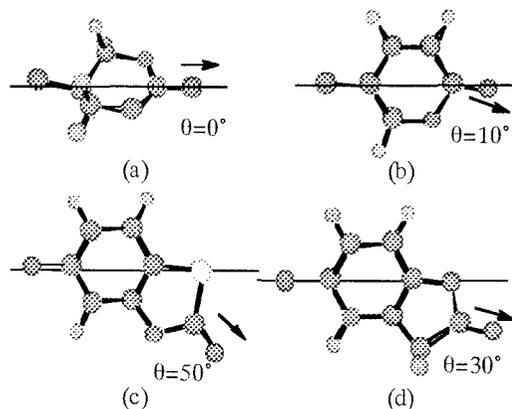


Fig. 3 Molecular geometry of terminal group for (a) **1**, (b) **2**, (c) **3** and **3'**, and (d) **4** and **4'**

As can be seen from comparison with Tables II, III and Fig. 3, the dielectric properties seem to be influenced not only by the geometrical circumstances around the carbonyl group but also the physical properties of the entire molecule and LC solvents.

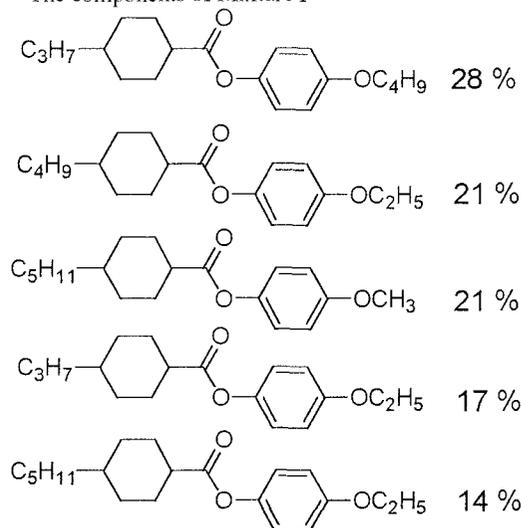
Conclusively, the LC compounds incorporating the carbonyl group such as lactone and carbonate at the terminal of the LC core have high dielectric anisotropy and useful for device materials.

4. ACKNOWLEDGEMENT

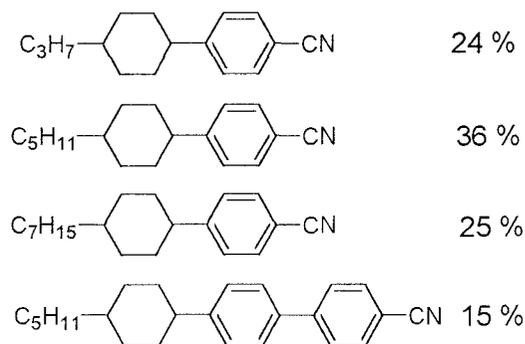
The authors are grateful to Chisso Petrochemical Corporation for the measurements of dielectric anisotropy.

5. FOOTNOTES

* The components of Mixture I



** The components of Mixture II



6. REFERENCES

- [1] L. Pohl and U. Finkenzerler, "Liquid Crystals, Application and Uses", Ed. by B. Bahadur, World Scientific, Singapore (1990) p.140.
- [2] H. Okamoto, T. Okamoto, and S. Takenaka, *Chem. Lett.*, **2000**, 1040-1041.
- [3] H. Okamoto, T. Okamoto, V. F. Petrov, and S. Takenaka, *Mol. Cryst. Liq. Cryst.*, **364**, 719-725 (2001).
- [4] S. Takenaka and H. Okamoto, Jpn. Kokai Tokkyo Koho (2002). JP 2002088078.

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