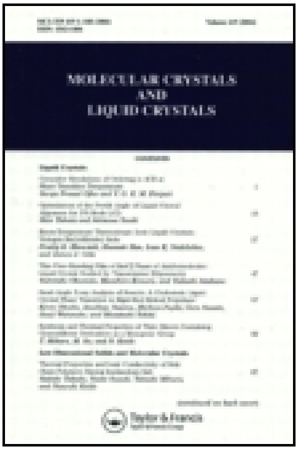

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Synthesis and Physical Properties of Liquid Crystals with a Carbonyl Group at the Terminal Position

Hiroaki Okamoto [a], Tsuyoshi Okamoto [a], Vladimir F. Petrov [a] & Shunsuke Takenaka [a]

[a] Faculty of Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi, 755-8611, JAPAN

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Synthesis and Physical Properties of Liquid Crystals with a Carbonyl Group at the Terminal Position

HIROAKI OKAMOTO, TSUYOSHI OKAMOTO, VLADIMIR F. PETROV and SHUNSUKE TAKENAKA

Faculty of Engineering, Yamaguchi University, Tokiwadai 2–16–1, Ube, Yamaguchi 755–8611, JAPAN

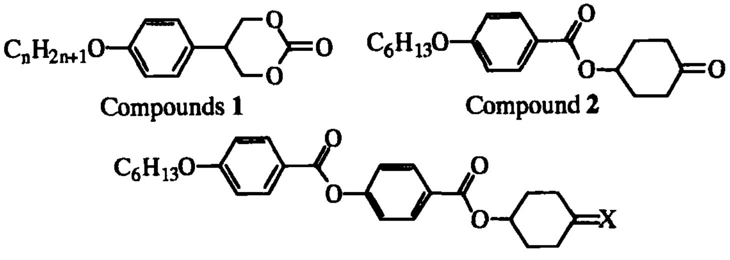
This paper describes the synthesis and physical properties of some polar liquid crystalline compounds having a 1,3-dioxan-2-one or a cyclohexanone at the terminal position. The mesomorphic properties of both compounds are discussed in terms of their geometrical characteristics.

Keywords: Liquid Crystals; Terminal Carbonyl Group; Smectic A Phase; Synthesis; Phase Diagram

INTRODUCTION

Recently, liquid crystals with positive dielectric anisotropy are required as the components of liquid crystalline materials for twisted nematic (TN) and super twisted nematic (STN) display applications. For this purpose, many liquid crystals having a terminal polar substituent such as a cyano group, a nitro one, or fluorine atom have been extensively developed.[1]

It is well known that carbonyl and carbonate groups have a large dipole moment similar to the cyano and nitro ones. In order to determine the physico-chemical properties of the terminal carbonyl and carbonate groups on the liquid crystalline molecules, some new series of liquid crystalline compounds **1–3** have been synthesized.



Compounds **1**

Compound **2**

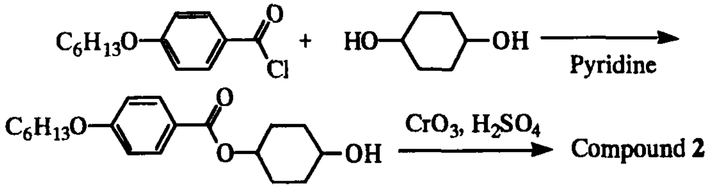
Compound **3a** X=H, OH (*cis*)
3b X=OH, H (*trans*)
3c X=O

FIGURE 1 Chemical structures for compounds **1**–**3**

RESULTS AND DISCUSSION

Synthesis

Compounds **1** were prepared by the method described in our earlier paper.[2] Compounds **2** and **3** were prepared according to Scheme.



Scheme Synthesis of compound **2**

The chemical structures of **1**–**3** were confirmed by ^1H NMR and IR spectroscopies. In our earlier study [2], the 4-alkoxyphenyl group for **1** possessed an equatorial position of the 1,3-dioxan-2-one with a boat form. The ^1H NMR spectra of **3a** shows a multiplet at 5.15 ppm assigned to the methine proton at the juncture of the benzoate and the cyclohexanol. The coupling pattern of the methine proton is probably due to the equilibrium between chair and boat forms.[3] On the other hands, the signal of the methine proton of **3b** is observed in the NMR spectra at 5.03 ppm with a triple-triplet (*J*=9.5 and 3.5 Hz) coupling pattern. These coupling constants indicate the methine proton possesses an axial position with a chair form of the cyclohexane ring, so that **3b** has a chair form, where both substituents on the cyclohexane ring have equatorial position. For **3c**, the coupling pattern and constants (*J*=5.5 and 3.0 Hz) of the methine proton indicate an axial–equatrial and equatorial–equatrial couplings, so that the methine proton possesses the equatorial position. As the results, the 4–X-benzoyloxy group possesses the axial position on the cyclohexanone ring.

These results suggest that the molecular geometries of **1** and **3b** have linear molecular structures. On the other hand, **2** and **3c** have bent structures on the cyclohexanone ring.

Physical Properties

Transition temperatures and latent heats for **1–3** are summarized in Table 1.

TABLE 1 Transition temperatures and latent heats for **1–3**

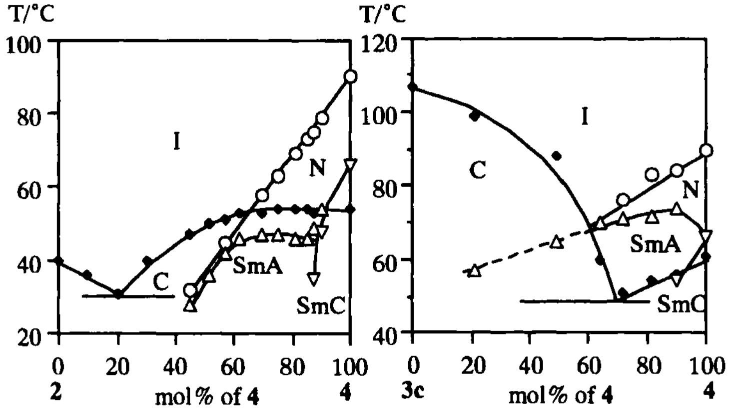
		Transition temperatures (°C)							Latent heats (kJ/mol)		
	n	C		SmA		N		I	mp	SmA–I	N–I
1a	3	•	100	–		–		•	27.6		
1b	4	•	86	–		–		•	27.3		
1c	5	•	60	(•	12)	–		•	30.2	0.77	
1d	6	•	61	(•	39)	–		•	23.7	1.64	
2	6	•	44	–		[•	–15]	•	26.0		
3a	6	•	98	–		–		•			
3b	6	•	127	–		(•	117)	•	37.0		2.1
3c	6	•	108	[•	50]	–		•	37.0		

C, SmA, N, and I indicate crystal, smectic A, nematic, and isotropic phases, respectively. Parentheses and brackets indicate monotropic and virtual transitions, respectively.

Compounds **1c** and **1d** show a monotropic smectic A phase with a focal conic fan texture as mentioned our earlier paper [2]. Compounds **2**, **3a**, and **3c** do not show any mesophase, even on a rapid cooling process. On the other hand, **3b** shows a monotropic nematic phase with a schlieren texture on the homogeneous alignment glass surface. These results indicate that the molecular geometry plays an important role for mesomorphic properties as mentioned above.

In order to determine the mesomorphic properties of **2** and **3c**, we examined binary phase diagrams with a non-polar liquid crystal, 4-hexyloxyphenyl 4-octyloxybenzoate (**4**) [4], as shown in Figure 2. As we can see from Figure 2, the virtual N–I and SmA–I transition temperatures for **2** and **3c** are ca. –15 °C and 50 °C, respectively. These results are consistent with the fact that the molecular geometries for **2** and **3c** have the bent structures as mentioned above.

Interestingly, the enhanced SmA phases are recognized around 70mol% of **4** for Figure 2(a) and 90mol% of **4** for Figure 2(b). These phase behaviors were often observed in polar–nonpolar liquid crystal mixtures.[5] Therefore, these results indicate that **2** and **3c** have a polar nature.



(a) (b)

FIGURE 2 Binary phase diagrams for the mixtures of (a) **2** – **4** and (b) **3c** – **4**.

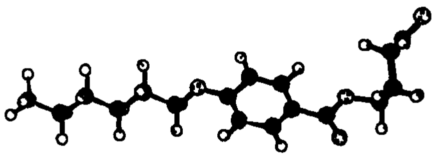


FIGURE 3 Molecular structure for compound **2**

The dipole moment calculated by a semi-empirical molecular orbital calculation is 4.7 D for **2**, where the most stable molecular structure with the axial substituted cyclohexanone were calculated by an AM1 method, as shown in Figure 3. Similar calculations for **1c** and **3c** give the dipole moment of 7.2 D [2] and 6.6 D, respectively.

Considering the phase diagrams and the dipole moments, **2** and **3c** exhibit the polar nature similar to **1**.

CONCLUSION

The new series of the liquid crystalline compounds **1–3** having a carbonyl or a carbonate group at the terminal position were synthesized. Compounds **1** show the smectic A phase. Compounds **2** and **3c** having a cyclohexanone at the terminal position were non-mesogenic due to their bent structures. However, they are expected to be a polar component for the display applications.

EXPERIMENTAL

Method

The purity of materials was confirmed by HPLC, ^{1}H NMR spectroscopy, and DSC thermogram using a "DSCPURITY" program (Seiko-denshi Co.). The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J/g). The DSC thermogram was operated at a heating or a cooling rate of 5 °C/min. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). The molecular geometry and parameters used in this paper were calculated by a semi-empirical molecular orbital calculation for a single molecule, using the AM1 method.

Materials

Compounds **1** were synthesized according to our earlier paper [2].

4-Hydroxycyclohexyl 4-hexyloxybenzoate

To a solution of 1,4-cyclohexanediol (*cis-trans* mixture) (4.2 g) in dry pyridine (80 ml), 4-hexyloxybenzoyl chloride (4.1 g) in toluene (20 ml) was added at room temperature. The reaction mixture was stirred at 70 °C for 5 h. The solvent was evaporated and the residue was purified by column chromatography on silica gel, yielding 3.2 g (56%)

of the *cis-trans* mixtures of cyclohexanol derivative. IR : ν=3425 and 1711 cm^{-1}, ^{1}H NMR: δ=0.91 (3H, t, *J*=6.8 Hz), 1.31–1.85 (13H, m), 2.00–2.14 (4H, m), 3.76–3.83 (1H, m), 4.00 (2H, t, *J*=6.6 Hz), 4.95 (0.5H, m), 5.11 (0.5H, m), 6.90 (1H, d, *J*=8.0 Hz), 6.92 (1H, d, *J*=8.0 Hz), 7.96 (1H, d, *J*=8.0 Hz), and 8.00 (1H, d, *J*=8.0 Hz) ppm.

4-(4-Hexyloxybenzoyloxy)cyclohexanone (**2**)
To the solution of the cyclohexanol derivatives (1.1 g) in ether (20 ml), $K_2Cr_2O_7$ (0.6 g) in sulfuric acid (3M, 3 ml) was added dropwise at 0 °C. After stirring at room temperature for 2 h, the organic layer was separated and washed with aq. $NaHCO_3$ and brine. The solvent was evaporated and the residue was purified by column chromatography on silica gel and recrystallization from hexane-toluene, yielding 0.8 g (71%) of **2**. IR: ν=1708 cm^{-1}, ^{1}H NMR: δ=0.91 (3H, t, *J*=6.9 Hz), 1.31–1.52 (6H, m), 1.81 (2H, quin, *J*=6.9 Hz), 2.10–2.29 (4H, m), 2.31–2.48 (2H, m), 2.60–2.71 (2H, m), 4.02 (2H, t, *J*=6.9 Hz), 5.40 (1H, tt, *J*=5.6, 3.6 Hz), 6.93 (2H, d, *J*=9.0 Hz), and 8.00 (2H, d, *J*=6.9 Hz) ppm.

Compounds **3a**, **3b**, and **3c**
Compounds **3a**, **3b**, and **3c** were synthesized according to **2**. **3a** and **3b** were separated by column chromatography on silica gel, respectively.

3a, IR: ν=3398, 1724, and 1714 cm^{-1}, ^{1}H NMR: δ=0.92 (3H, t, *J*=6.9 Hz), 1.33–1.51 (6H, m), 1.69–1.87 (8H, m), 2.01–2.09 (2H, m), 3.84 (1H, m), 4.05 (2H, t, *J*=6.6 Hz), 5.15 (1H, m), 6.98 (2H, d, *J*=9.0 Hz), 7.28, (2H, d, *J*=9.0 Hz), 8.12 (2H, d, *J*=9.0 Hz), and 8.13 (2H, d, *J*=9.0 Hz) ppm.

3b, IR: ν=2428, 1732, and 1718 cm^{-1}, ^{1}H NMR: δ=0.92 (3H, t, *J*=6.9 Hz), 1.33–1.70 (6H, m), 1.83 (2H, qui., *J*=6.5 Hz), 2.03–2.15 (4H, m), 3.82 (1H, m), 4.05 (2H, t, *J*=6.5 Hz), 5.03 (1H, tt, *J*=9.5 and 3.5 Hz), 6.98 (2H, d, *J*=9.0 Hz), 7.28 (2H, d, *J*=9.0 Hz), 8.10 (2H, d, *J*=9.0 Hz), and 8.13 (2H, d, *J*= 9.0 Hz) ppm.

3c, IR: ν=1733 and 1709 cm^{-1} ^{1}HNMR: δ=0.92 (3H, t, *J*=6.9 Hz), 1.33–1.55 (6H, m), 1.93 (2H, qui., *J*=6.6 Hz), 2.12–2.33 (4H, m), 2.46 (2H, m), 2.65 (2H, m), 5.45 (1H, tt, *J*=5.5 and 3.0 Hz), 6.99 (2H, d, *J*=9.0 Hz), 7.31 (2H, d, *J*=9.0 Hz), 8.12 (2H, d, *J*=9.0 Hz), and 8.13 (2H, d, *J*=9.0 Hz) ppm.

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