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Synthesis and Characterization of Novel All-Organic Liquid Crystalline Radicals

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*We have synthesized a new series of all-organic liquid crystalline (LC) radical compounds (**2**), which are the structural isomers of the previously reported series (**1**) containing a chiral nitroxide unit in the mesogen core. Only difference between the two isomers is the orientation in the ester functionality (–OCO– vs –COO–). The new LC compounds **2** with C4 to C8 alkoxy terminal chains showed the distinct odd-even effects of alkoxy terminal chains with respect to the thermal stability of nematic phases, while such effects were not observed for the isomers **1**.*

Keywords: chiral nitroxide; nematic phase, nitroxyl radical; odd-even effects; paramagnetic liquid crystals

INTRODUCTION

Paramagnetic calamitic liquid crystals have attracted great interest due to the possibility of orientation control of LC molecules by weak

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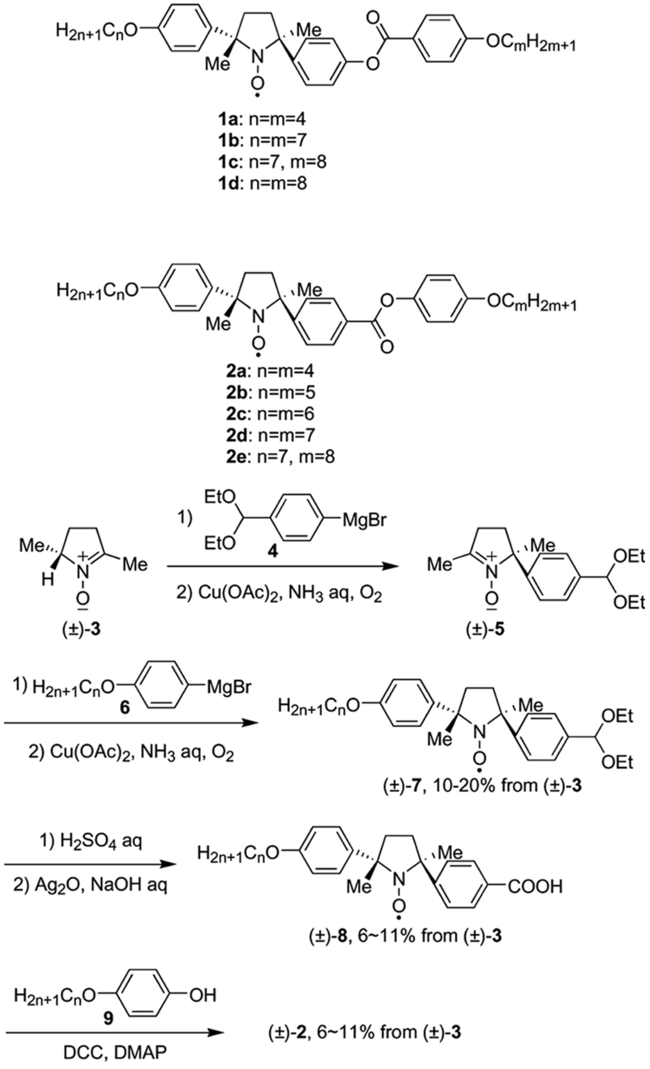
magnetic fields [1,2] and the use as LC spin probes for electron paramagnetic resonance (EPR) spectroscopic studies to observe the dynamic behavior of diamagnetic liquid crystals. The paramagnetic liquid crystals are classified into two categories; one is a metallomesogen containing a paramagnetic metal ion and the other is an organic radical mesogen. The former metallomesogens can have a large paramagnetic susceptibility anisotropy ($\Delta\chi_{\mathrm{para}}$) which originates from the d- or f-metal ion and seems advantageous to the orientation control of LC molecules by magnetic fields [3–6]. On the other hand, the latter organic mesogens are appropriate for the LC spin probes to investigate the orientation of the diamagnetic organic LCs, due to their low viscosity and very small $\Delta\chi_{\mathrm{para}}$ which does not disturb the $\Delta\chi_{\mathrm{dia}}$-controlled orientation of diamagnetic organic liquid crystals [7], if the spin source moiety is fixed in the mesogen core so as to avoid the free rotation inside the molecule.

We successfully synthesized the first all-organic paramagnetic LC compounds **1** [8–10], which contain a chiral nitroxide unit in the mesogen core. The racemic or enantiomerically-enriched **1** exhibited N or N*, and/or SmC or SmC* phases, respectively. Noteworthy is the fact that the chiral SmC* phase of **1** showed a ferroelectricity [9,10].

In order to investigate the influence of the direction and magnitude of molecular electric dipole moments on the stability of LC phases, we have modified the molecular structure of **1** and prepared a series of 4-alkoxyphenyl 4-[5-(4-alkoxyphenyl)-2,5-dimethylpyrrolidine-1-oxyl-2-yl]benzoate (**2**) (Scheme 1). Here we report the preparation and characterization of the new LC compounds (±)-**2** with C4 to C8 alkoxy terminal chains.

EXPERIMENTAL

Unless otherwise noted, solvents and reagents were reagent grade and used without further purification. Tetrahydrofuran (THF) which is used for EPR spectral measurement or Grignard reactions was distilled from sodium/benzophenone ketyl under argon. Dichloromethane (DCM) for esterification reaction was distilled from calcium hydride under argon. Phase transition temperatures were determined by differential scanning calorimetry (DSC) (SHIMADZU DSC-50) and polarized optical microscopy (Olympus BHSP). Hot-stage (JHC TH-600PH) was used as the temperature control unit for the microscopy. IR spectra were recorded with SHIMADZU IRPrestige-21. EPR spectra were recorded with a JEOL FE1XG. Magnetization was recorded with QUANTUN DESIGN MPMS-2 and MPMS-5S. For variable-temperature X-ray diffraction measurement, the data collections were performed on a Rigaku RINT2200/PC-LH diffractometer.



SCHEME 1 Molecular structures of (±)-**1** and (±)-**2**, and synthesis of (±)-**2**.

General Synthetic Procedure of (±)-2 (Scheme 1)

Aryl Magnesium Bromide (4, 6)

To magnesium turnings (0.243 g, 10 mmol) dried by heating at 3 mmHg was added THF (10 mL), arylbromide (10 mmol), and a small amount of iodine under argon. The reaction started by heating, and the reaction mixture was refluxed for 4 h to afford a solution of aryl magnesium bromide in THF.

2,5-Diaryl-2,5-dimethylpyrrolidine-1-oxyl Radical (7) [8–11]

To a stirred solution of the freshly prepared Grignard reagent **4** (10 mmol) in THF (10 mL) was slowly added a solution of the nitrone **3** (5.0 mmol) in THF (10 mL) under argon at -78°C. The temperature was raised slowly to room temperature, and stirring was continued overnight. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (50 mL), and then extracted with DCM (2×50 mL). The combined DCM extract was dried over $MgSO_4$ and evaporated. The residual oil was dissolved in methanol (20 mL). To this solution were added aqueous NH_3 solution (25 wt%, 1.4 ml) and cupper (II) acetate monohydrate (0.160 g, 0.80 mmol). Oxygen was bubbled through the yellow solution until a persistent deep blue color developed. The solvent was then removed under reduced pressure and the crude product was redissolved in DCM (50 mL). This solution was washed with saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, and evaporated. The water was removed by the azeotropic method with benzene and the remaining trace of benzene was removed in vacuo. The crude product **5** was dissolved in THF (10 mL) and reacted with the freshly prepared Grignard reagent **6** (the same quantity and conditions as described above). After a similar workup procedure, the crude product was obtained. It was again oxidized by O_2/cupper acetate. Purification by column chromatography (hexane/ether) on silica gel provided the nitroxyl radical **7**.

2-(4-Alkyloxyphenyl)-5-(4-hydroxycarbonylphenyl)-2,5-dimethylpyrrolidine-1-oxyl Radical (8)

To a solution of **7** (1.0 mmol) in THF (2 ml) was added aqueous H_2SO_4 (5%; 0.50 mL) and the mixture was stirred for 8 h at room temperature. Brine and DCM were then added. The organic phase was separated, dried over $MgSO_4$, and evaporated. To a vigorously stirred suspension of Ag_2O (463 mg, 2.0 mmol) in aqueous NaOH solution (10%, 4 mL) was added the crude product in THF (1.5 mL) at 60°C, and the mixture was stirred under reflux for 40 min. After cooling, the reaction mixture was acidified with aqueous H_2SO_4 (5%) to pH 2, and extracted with $CHCl_3$ (3×10 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (DCM/ether) to give carboxylic acid (±)-**8**.

(±)-**8a**: Mp 172.8–173.0°C. EPR: $g = 2.0058$, $a_N = 1.33$ mT. IR (DIFFUSE REFLECTION): ν 2927, 2867, 1685, 1604, 1570, 1506, 1420, 1279, 1242, 1180, 1067, 845, 779, 712 cm^{-1}. Anal. Calcd for $C_{23}H_{28}NO_4$: C, 72.23; H, 7.38; N, 3.66; Found: C, 72.05; H, 7.47; N, 3.49.

(±)-**8b**: Mp 170.5–171.5°C. EPR: $g = 2.0056$, $a_N = 1.34$ mT. IR (DIFFUSE REFLECTION): ν 2937, 2872, 1689, 1607, 1570, 1510, 1424, 1289, 1247, 1185, 1051, 839, 780, 707 cm^{-1}. Anal. Calcd for $C_{24}H_{30}NO_4$: C, 72.70; H, 7.63; N, 3.53; Found: C, 72.89; H, 7.62; N, 3.48.

(±)-**8c**: Mp 168.4–169.3°C. EPR: $g = 2.0059$, $a_N = 1.33$ mT. IR (DIFFUSE REFLECTION): ν 2949, 2859, 1684, 1606, 1571, 1505, 1424, 1290, 1247, 1182, 1075, 839, 780, 708 cm^{-1}. Anal. Calcd for $C_{25}H_{32}NO_4$: C, 73.14; H, 7.86; N, 3.41; Found: C, 73.04; H, 7.81; N, 3.31.

(±)-**8d**: Mp 168.3–169.2°C. EPR: $g = 2.0055$, $a_N = 1.34$ mT. IR (DIFFUSE REFLECTION): ν 2919, 2853, 1685, 1607, 1570, 1507, 1424, 1285, 1247, 1185, 1074, 840, 780, 707 cm^{-1}. Anal. Calcd for $C_{26}H_{34}NO_4$: C, 73.55; H, 8.07; N, 3.30; Found: C, 73.69; H, 8.01; N, 3.22.

General Procedure for Esterification to Give 2 [12]

Under argon, a 10 ml of oven-dried, round-bottomed flask containing anhydrous DCM (3 ml) is charged with the carboxylic acid (±)-**8** (0.2 mmol), the phenol **9** (0.2 mmol) [13], dicyclohexylcarbodiimide (DCC, 0.22 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.04 mmol). After the mixture was stirred for 12 h at room temperature, the precipitated white solid was removed by filtration, and the filtrate was evaporated. The residue was purified by flash column chromatography (hexane/ether) to afford the ester (±)-**2**.

(±)-**2a**: EPR: $g = 2.0058$, $a_N = 1.34$ mT. IR (DIFFUSE REFLECTION): ν 2929, 2876, 1735, 1608, 1505, 1271, 1247, 1183, 1074, 839, 770, 703 cm^{-1}. Anal. Calcd for $C_{33}H_{40}NO_5$: C, 74.69; H, 7.60; N, 2.64; Found: C, 74.30; H, 7.69; N, 2.65.

(±)-**2b**: EPR: $g = 2.0056$, $a_N = 1.34$ mT. IR (DIFFUSE REFLECTION): ν 2937, 2871, 1738, 1609, 1511, 1279, 1254, 1184, 1078, 830, 771, 705 cm^{-1}. Anal. Calcd for $C_{35}H_{44}NO_5$: C, 75.24; H, 7.94; N, 2.51; Found: C, 75.01; H, 8.01; N, 2.16.

(±)-**2c**: EPR: $g = 2.0058$, $a_N = 1.34$ mT. IR (DIFFUSE REFLECTION): ν 2928, 2855, 1730, 1609, 1507, 1280, 1244, 1078, 834, 771, 705 cm^{-1}. Anal. Calcd for $C_{37}H_{48}NO_5$: C, 75.73; H, 8.25; N, 2.39; Found: C, 75.78; H, 8.30; N, 2.38.

(±)-**2d**: EPR: $g = 2.0059$, $a_N = 1.33$ mT. IR (DIFFUSE REFLECTION): ν 2935, 2857, 1730, 1608, 1507, 1278, 1247, 1186, 1076, 833, 771, 705 cm^{-1}. Anal. Calcd for $C_{39}H_{52}NO_5$: C, 76.19; H, 8.40; N, 2.28; Found: C, 75.95; H, 8.40; N, 2.29.

(±)-**2e**: EPR: $g = 2.0060$, $a_N = 1.31$ mT. IR (DIFFUSE REFLECTION): ν 2920, 2854, 1734, 1608, 1507, 1268, 1249, 1184, 1073, 858, 770, 707 cm^{-1}. Anal. Calcd for $C_{40}H_{54}NO_5$: C, 76.40; H, 8.66; N, 2.23; Found: C, 76.31; H, 8.51; N, 2.26.

RESULTS AND DISCUSSION

The magnetic properties of (±)-**2** are summarized in Table 1. The EPR spectra were measured in THF at a field of 0.34 T at 25°C, displaying an intense 1:1:1 triplet. The magnetic susceptibility was measured in a quartz tube (3.5 $\phi \times 40$ mm) on a SQUID magnetometer at a field of 0.5 T in the temperature range 2–300 K, showing the existence of very weak antiferromagnetic intermolecular interactions ($\theta < 0$). The Curie constants indicate that the radical purity of (±)-**2** is very high.

The phase transition behavior of (±)-**2** is characterized by DSC analysis and polarized optical microscopy (Table 1 and Fig. 1). All of (±)-**2** showed a Schlieren or thread-like texture typical of a nematic phase under planar boundary conditions by hot-stage polarized microscopy (Fig. 2) [14]. These nematic phases were observed over a wide temperature range during the cooling process, and the phases of (±)-**2b** were monotropic. Variable temperature X-ray diffraction analyses of (±)-**2** verified the existence of nematic phases, showing only a halo.

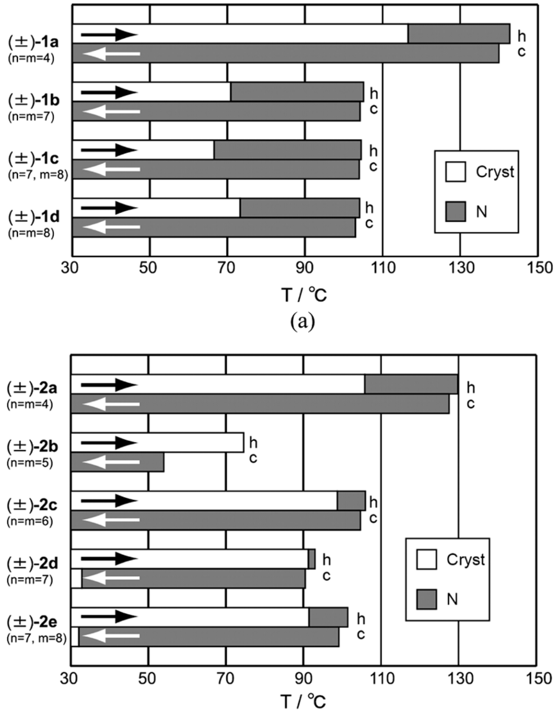
Compounds (±)-**2** with C4 to C8 alkoxy terminal chains exhibited the distinct odd-even effects of alkoxy terminal chains with respect to the thermal stability of nematic phases; (±)-**2a** and (±)-**2c** with respective C4 and C6 alkoxy terminal chains showed the higher clearing points and the wider temperature ranges of the nematic phases than (±)-**2b** and (±)-**2d** with respective C5 and C7 terminal chains (Fig. 1). Furthermore, when one of the two C7 terminal chains of (±)-**2d**was lengthened by one carbon, the resultant (±)-**2e** with C7 and C8 terminal chains-showed a higher clearing point and a wider temperature range of the nematic phase than (±)-**2d**. These phenomena were often observed for the LC compounds showing a nematic phase [15].

Such odd-even effects of alkoxy terminal chains were not observed for (±)-**1**, the structural isomers of (±)-**2**. This result indicates that the origin of the observed odd-even effects seems to be related to the thermal stability of nematic phases (Fig. 1). As a preliminary study, it has been found that the molecular electric dipole moments of (±)-**2**, which have been calculated by the PM3 method after optimization of the molecular structures, are smaller by ca. 1 Debye than those of (±)-**1**. Therefore, it is conceivable that the weak intermolecular electric dipole-dipole interactions in the nematic phases of (±)-**2** allow the appearance of the odd-even effects which are sensitive to the surroundings.

TABLE 1 Magnetic Properties and Phase Transition Behavior of (±)-**2a–e**

	EPR[a]		SQUID		
Compound	g	a_N [mT]	C [emu K mol^{-1}][b]	θ [K][c]	Phase transition behavior[d] [°C] (H [kJ mol^{-1}])
(±)-**2a** (n = m = 4)	2.0058	1.34	0.37	−0.83	C 106 (21.1) N 130 (1.7) I
(±)-**2b** (n = m = 5)	2.0056	1.34	0.38	−0.02	C 62 (34.5) C 75 (2.78) (N 54 (0.1))[e] I
(±)-**2c** (n = m = 6)	2.0058	1.34	0.36	−0.30	C 99 (35.5) N 106 (2.29) I
(±)-**2d** (n = m = 7)	2.0058	1.33	0.38	−0.28	C 91 (-)[f] N 93 (2.0) I
(±)-**2e** (n = 7, m = 8)	2.0060	1.31	0.38	−0.01	C 91 (27.8) N 101.4 (1.7) I

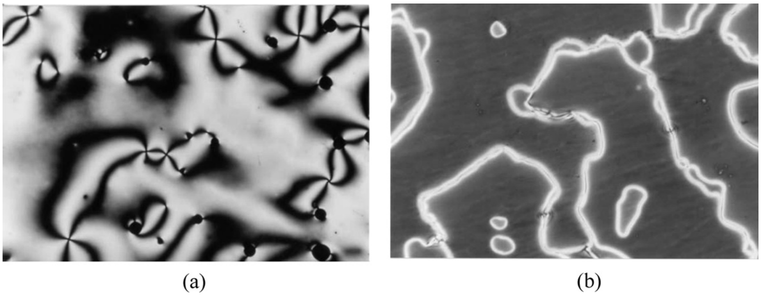
[a] Measured in THF at 25°C. [b] Curie constant. [c] Weiss temperature. [d] Determined by DSC analysis upon heating. Standard notation gives the transition temperatures between the crystalline (C), nematic (N), and isotropic (I) states. [e] The phase in a parenthesis emerges only upon cooling. [f] The phase transition is not observed by DSC analysis but by polarized microscopy.



(a)

(b)

FIGURE 1 Comparison of LC behavior of (±)-**2** with that of (±)-**1**. Transition temperatures determined by DSC analysis at a scanning rate of 5°C min^{-1} upon the heating (h) and cooling (c) processes. At this scanning rate, hysteresis is observed for the N-I or C-N phase transition between the heating and cooling runs, as is likely since thermal equilibrium is not reached during the measurement.



(a) (b)

FIGURE 2 Polarized optical micrographs showing (a) a Schlieren texture at 104.0°C and (b) a thread-like texture in a sandwich cell (50 μm)at 100.0°C, for (±)-**2c** under planar boundary conditions.

CONCLUSION

We have synthesized the racemates of novel mesogenic nitroxyl radicals **2** which contain a chiral nitroxide unit in the mesogen core. The racemic **2** bearing C4 to C8 alkoxy terminal chains showed a nematic phase over a wide temperature range during the cooling process and the odd-even effects of alkoxy terminal chains with respect to the clearing temperature and the temperature range of the nematic phase.

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