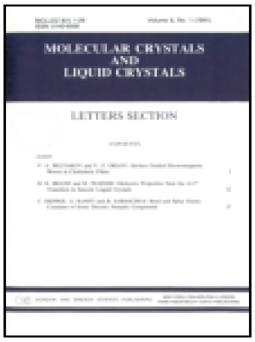

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Terminal Fluorinated Nitroxide Radical Liquid Crystalline Compounds

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We have synthesized a new series of all-organic paramagnetic liquid crystalline (LC) compounds, which include a five-membered ring nitroxide radical (NR) moiety in the mesogen core and fluorine atoms as terminal substituents. These new compounds are the structural analogs of the previously reported NR-LC compounds, and showed remarkable fluorine substituent effects. The introducing fluorine atom into terminal unit stabilizes nematic phase. However, an excess of fluorination leads to the destabilization of nematic phase.

Keywords paramagnetic liquid crystals; nitroxide radicals; molecular design; fluorine substituent effects; nematic phase

Introduction

Recently, molecular magnetic materials have attracted a great deal of attention. In contrast to inorganic solid-state materials including transition metals (Fe, Co, Ni, etc.) and/or lanthanides, molecular magnetic materials have some important characteristics as soft magnetic materials with fine-tunable magnetic properties and addable desired functions by molecular modification. The spin source of molecular magnetic materials is organic radical species and/or metal complexes. Since organic radicals are chemically unstable for functional materials because of their high reactivity, steric protection of the radical moiety is needed to stabilize them. Thus, the bulkiness derived from the steric protection causes low spin density, and therefore, the intermolecular magnetic interactions in organic radical materials are relatively weaker than those in metal complex materials. However, since the organic radical materials are metal-free, they have greater potential as biocompatible magnetic soft materials than the metal complex materials [1], and also, they are more favorable from the point of view of the element strategy.

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As one of the metal-free magnetic soft materials, nitroxide radical (NR) liquid crystalline (LC) compound **1** containing a five-membered ring NR moiety in the mesogen core has been reported [2]. This compound exhibits some fascinating properties in the externally applied magnetic fields [3]. For example, their molecular reorientation occurs in a uniform magnetic field and the motion of magnetic LC droplet occurs in a magnetic-field gradient [4, 5]. In addition, the increase of magnetic susceptibility at a crystalline (Cr)-to-LC phase transition of compound **1** has been observed (magneto-LC effects) [6]. The magneto-LC effects depend on the molecular structures and the LC phases; enantiomerically enriched NR-LC compounds show chiral LC phases and stronger magneto-LC effects than the corresponding racemates [7], and hydrogen-bonded all-organic NR-LC compounds show twice as strong magneto-LC effects as compound **1** [8].

Some other desired functions can be added to NR-LC materials easily by structural modification; for example, the ferroelectric-paramagnetic LC materials have been reported [9]. To obtain comprehensive molecular design strategy for any desired properties, we have to understand the relationship between the molecular structure and physical properties. However, the relationship for NR-LC compounds has not been understood completely. As one of the important properties, we focus on the stability of the LC phases. It has been reported that NR compounds analogous to compound **1** show several LC phases such as nematic (N) [2], smectic A (SmA) [7], smectic C (SmC) phases [9], etc. The phase transition behavior of NR-LC compounds undergoes unexpected changes depending on the length of side chains and the sort of binding groups. It is difficult now to predict the phase transition behavior of NR compounds exactly.

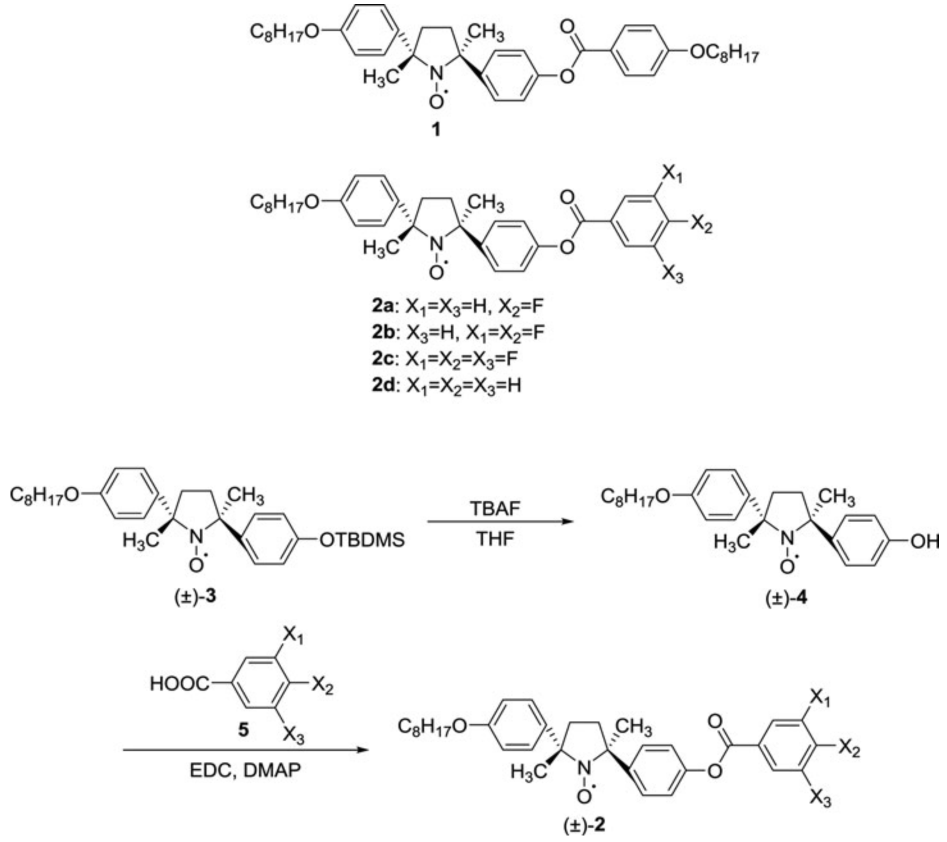
Generally, fluorine substituents are employed in LC structures to modify melting points, mesophase morphology, transition temperatures, and the many essential physical properties of LC materials, such as optical, dielectric and visco-elastic properties [10]. The small size of the fluorine substituent enables its incorporation into all types of LC phases without disrupting the LC nature of the materials; low-molecular weight or polymeric calamitic or discotic thermotropic or lyotropic phases. Fluorine atoms are commonly introduced into terminal substituents, lateral substituents and linking groups [10]. Here, we report the synthesis of NR-LC compounds with or without fluorine atoms as terminal substituents (±)−**2a–d** and the effects of the introduction of fluorine atoms into the NR-LC compounds.

Experimental

Unless otherwise noted, solvents and reagents were reagent grade and used without further purification. Tetrahydrofuran (THF) that is used for electron paramagnetic resonance (EPR) spectral measurement or Grignard reactions was distilled from sodium/benzophenone ketyl under nitrogen. Phase transition temperatures were determined by differential scanning calorimetry (DSC) (SHIMADZU DSC-60) and polarized optical microscopy (Olympus BX51). A hot stage (Japan High Tech, 10083) was used as the temperature control unit for the microscopy. IR spectra were recorded with SHIMADZU IRAffinity-1. EPR spectra were recorded with a JEOL JES-FA200. For variable temperature X-ray diffraction measurement, the data collections were performed on a Philips X'Pert-MPD diffractometer using Cu-Kα radiation with 1.5418 Å.

General Synthetic Procedure of Compounds (±)−2a–d (Scheme 1)

Compound (±)−**3** was prepared as the previous reported procedure [11].



Scheme 1. Molecular structures of (±)−**1** and (±)−**2a–d**, and synthesis of (±)−**2a–d**.

Deprotection of Tert-butyldimethylsilyl Group to Give Compound 4

To (±)−**3** (1.5 mmol) dissolved in THF (50 mL) was added 2 mL of tetrabutylammonium fluoride (TBAF, 1 M solution in THF) at 0°C. After stirring for 20 min, saturated aqueous NH_4Cl (50 mL) was added. The reaction mixture was extracted with ether (50 mL × 2) and washed with saturated aqueous $NaHCO_3$ (50 mL). The combined organic phase was dried over $MgSO_4$ and evaporated. Flash column chromatography (silica gel, hexane/ethylacetate = 8/2) of the residue gave (±)−**4** as yellow crystals.

General Procedure for Esterification to Give Compound 2

DCM (50 mL) was charged with the phenol **4** (0.3 mmol), the carboxyl acid **5** (0.33 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 0.45 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.09 mmol). After the mixture was stirred for 12 h at room temperature, reaction solution was added saturated aqueous NH_4Cl (50 mL), and

Table 1. Magnetic properties and phase transition behaviors of (±)−**2a–d**

Compound	EPR[a] *g*	a_N [mT]	Phase transition behavior[b] [°C]
(±)−**2a**	2.0059	1.33	Cr 85.33 (N 83.31) Iso
(±)−**2b**	2.0059	1.33	Cr 83.87 (N 60.02) Iso
(±)−**2c**	2.0059	1.34	Cr 80.75 Cr 83.06 Cr 88.73 (N 39.17) Iso
(±)−**2d**	2.0060	1.35	Cr 60.06 Iso

[a] Measured as THF solutions at room temperature.

[b] Determined by DSC analysis upon heating and cooling processes. Standard notation gives the transition temperatures between the crystalline (Cr), nematic (N) and isotropic (Iso) phases.

extracted with ether (50 mL × 2). The extract was dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ether = 8/2) to afford the ester (±)−**2a–d** as yellow crystals. The yields of (±)−**2a–d** from (±)−**4** is about 70% regardless of fluorine substitutions.

(±)−**2a**: IR (KBr) ν 2930, 1738, 1603, 1508, 1471, 1267, 1202, 1174, 1151, 1072, 837, 762 cm^{-1}. Anal. Calcd. for $C_{33}H_{39}FNO_4$: C, 74.41; H, 7.38; N, 2.63; Found: C, 74.41; H, 7.58; N, 2.62. HRMS (FAB+): Calcd. for $C_{33}H_{39}FNO_4$ $[M]^+$, 532.2863; Found, 532.2860.

(±)−**2b**: IR (KBr) ν 2924, 1738, 1609, 1508, 1431, 1296, 1244, 1190, 1066, 932, 833, 756 cm^{-1}. Anal. Calcd. for $C_{33}H_{38}F_2NO_4$: C, 71.98; H, 6.96; N, 2.54; Found: C, 71.93; H, 6.82; N, 2.50. HRMS (FAB+): Calcd. for $C_{33}H_{38}F_2NO_4$ $[M]^+$, 550.2769; Found, 550.2772.

(±)−**2c**: IR (KBr) ν 2918, 1738, 1609, 1531, 1441, 1366, 1223, 1190, 1050, 955, 829, 754 cm^{-1}. Anal. Calcd. for $C_{33}H_{37}F_3NO_4$: C, 69.70; H, 6.56; N, 2.46; Found: C, 69.69; H, 6.76; N, 2.46. HRMS (FAB+): Calcd. for $C_{33}H_{37}F_3NO_4$ $[M]^+$, 568.2675; Found, 568.2666.

(±)−**2d**: IR (KBr) ν 2930, 1738, 1603, 1508, 1452, 1267, 1202, 1175, 1065, 1024, 835, 708 cm^{-1}. Anal. Calcd. for $C_{33}H_{40}NO_4$: C, 77.01; H, 7.83; N, 2.72; Found: C, 76.97; H, 8.00; N, 2.75. HRMS (FAB+): Calcd. for $C_{33}H_{40}NO_4$ $[M]^+$, 514.2957; Found, 514.2949.

Results and Discussion

The magnetic properties of (±)−**2a–d** are summarized in **Table 1**. Their *g* values and hyperfine coupling constants (a_N) were determined by EPR spectra, which were measured as THF solutions at a field of 0.33 T at room temperature, displaying an intense 1:1:1 triplet.

The phase transition behaviors of (±)−**2a–d** are characterized by DSC analysis and polarized optical microscopy (**Table 1** and **Fig. 1**). Compounds (±)−**2a–c** showed a Schlieren or thread-like texture typical of the N phase by hot-stage polarized optical microscopy (**Fig. 2**) [12]. These N phases were monotropic and observed over a wide temperature range during the cooling process. Meanwhile, compound (±)−**2d** did not exhibit textures typical of any LC phases. Variable temperature X-ray diffraction analyses of (±)−**2a–c** verified the existence of N phases, showing only a halo.

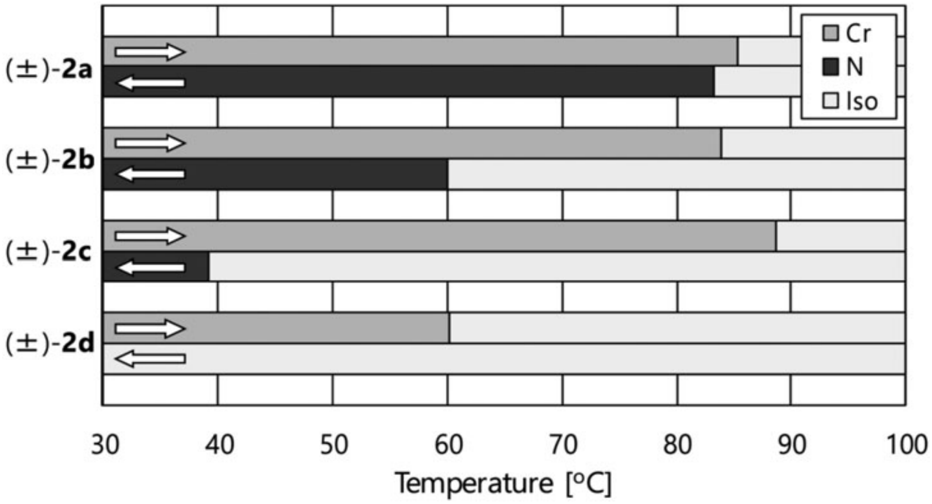


Figure 1. Comparison of LC phase behaviors of (±)−**2a–d**. Transition temperatures determined by DSC analysis at a scanning rate of 5°C/min upon the heating and cooling processes. During the cooling process, the supercooled N-to-Cr transition was observed and N phase was kept stable to around room temperature.

Fluorinated compounds (±)−**2a–c** showed the supercooled N-to-Cr transition in the cooling process (**Fig. 1**). In contrast, non-fluorinated compound (±)−**2d** did not exhibit any LC phases. We guess that this is because N phase is stabilized by dipole moments along to molecular long axis induced by C-F bond polarization. In fact, DFT calculations at B3LYP/6-31G** level using Gaussian 09 program package [13] show that dipole moments of the terminal aryl groups of the fluorinated compounds (±)−**2a–c**, fluorobenzene (1.348 D), 1,2-difluorobenzene (2.262 D) and 1,2,3-trifluorobenzene (2.581 D), are

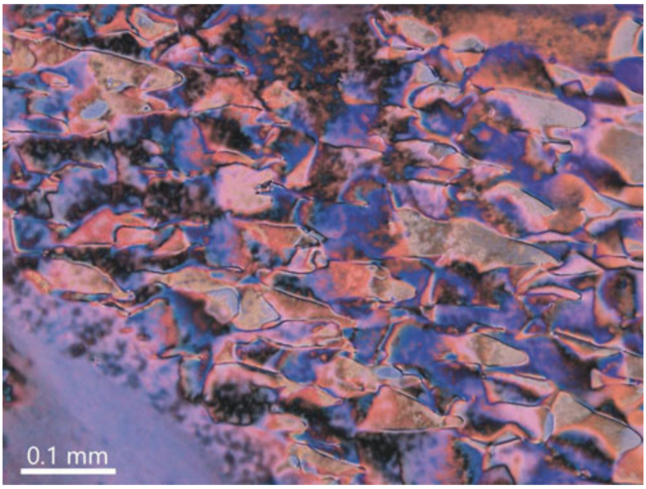
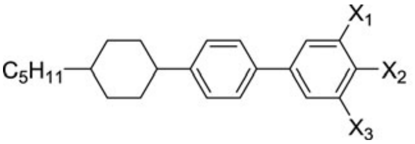


Figure 2. Polarized optical micrograph showing a thread-like texture on cooling process at 80°C, for (±)−**2a**.

Table 2. Phase transition behavior of the previously reported biphenylcyclohexane-based LC compounds[14]



5a: $X_1=X_3=H, X_2=F$
5b: $X_3=H, X_1=X_2=F$
5c: $X_1=X_2=X_3=F$

Compound	Phase transition behavior [°C]
5a	Cr 102.0 N 153.9 Iso
5b	Cr 55.0 N 105.4 Iso
5c	Cr 25.0 N 54.8 Iso

larger than that of the terminal aryl group of non-fluorinated compound (±)−**2d**, benzene (0.000 D).

However, an excess of fluorination is likely to cause destabilization of N phase. Difluorinated and trifluorinated compounds (±)−**2b** and (±)−**2c** have lower clearing points (Iso-to-N) than monofluorinated compound (±)−**2a**. For every introduction of a fluorine atom, clearing point drops by about 20°C (**Fig. 1**). Such fluorination effects of LC compounds were also observed for a typical biphenylcyclohexane-based mesogenic core structure **5a–c** (**Table 2**) [14]. It is most likely that the difference of molecular shape between (±)−**2a–d** does not play a role in the stability of N phase because van der Waals radius of fluorine atom (0.147 nm) is not so different from hydrogen atom (0.120 nm). We should consider that electric dipole-dipole interactions induced by C-F bond polarization alter the stability of N phase.

In contrast to the clearing points, the over-fluorinated effects on melting points were not observed. In case of above typical biphenylcyclohexane-based LC compounds 5a-c the terminal fluorinations induced depression of melting point as well as clearing point (**Table 2**) [14]. Meanwhile, compounds (±)-2a-c have almost the same melting points in spite of the difference of the number of fluorine atoms. These results indicate that the fluorine substituents in the terminal benzene ring little affect the melting points, and instead, the characteristic five-membered ring NR moiety plays an important role in molecular packing.

Conclusion

We have synthesized the racemates of novel NR compounds (±)−**2a–d**, which contain a chiral NR unit in the mesogen core and fluorine atoms as polar substituents in terminal unit. On the one hand, non-fluorinated compound (±)−**2d** does not show any LC phases. On the other hand, fluorinated compounds (±)−**2a–c** show N phase over a wide temperature range during the cooling process. These results indicate that the introducing first fluorine atom stabilizes N phases, but the additional fluorine substituents in terminal unit give rise to lower clearing point, namely, destabilize N phase. We believe that the phase transition behaviors of NR-LC compounds could be controlled by the proper fluorine substituents. To understand relationship between molecular structure and physical properties and to obtain some desired properties, additional works are needed to be performed, such as fluorine substituents in another position; lateral substituents, linking groups and so on.

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