Substituent effects on temperature range of liquid crystalline phases of nitroxide radical compounds

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All-organic paramagnetic liquid crystalline (PLC) materials with a five-membered ring nitroxide radical moiety in the mesogen core attract a great deal of attention because of their fascinating properties in externally applied magnetic fields.[1] For example, the molecular reorientation in a uniform magnetic field[2] and the motion of LC droplet in a magnetic-field gradient[3] have been reported. However, the way to design PLC nitroxide radical compounds exhibiting desired properties have not been established. As one of the important properties, we focus on the temperature ranges of the LC phases, which usually depend on lateral substituents and terminal groups. Here, we report the synthesis of novel PLC nitroxide radical compounds, which are analogues of the previously reported compound 1,[4] and the substituent effects on the temperature ranges of the LC phases.

PLC compounds synthesized in this study are shown in Figure 1. They have fluorine or hydrogen atoms as the lateral substituents, and alkoxy, alkyl, or cyano groups as the terminal groups. The phase transition behaviors were determined by polarizing microscopy and DSC analysis. To predict the stable conformations, DFT-optimization at B3LYP/6-31G* level was carried out.

LC phase temperature ranges are shown in Figure 2. The structure difference between 1 (oxygen) and 2 (methylene) in terminal chain leads to dramatic change in the temperature range of the LC phases. On the one hand, 1 exhibits the lowest melting point and the widest LC phase range in all compounds. On the other hand, 2 does not show any LC phases in the heating process. The stable conformation of ethoxybenzene calculated by DFT-optimization at B3LYP/6-31G* level shows that the ethoxy group could be in the same plane of benzene ring owing to their orbital overlapping (Figure 3). Therefore, 1 shows the most stable LC phase because of its more planar structure.[5]

Dipole moments also have an important role for LC phase stability of nitroxide radical compounds. Compounds containing a cyano group (3, 4) show relatively wide temperature ranges of the LC phases. These indicate that a large dipole moment of the cyano group along molecular long axis stabilizes LC phase. In contrast, introducing a fluorine atom to the lateral position makes the LC phase temperature range narrow (5) owing to a large dipole moment perpendicular to the molecular long axis arising from the C-F bond. However, introducing a fluorine atom would stabilize the LC phases for 4 and 6 by disturbing molecular packing. These results suggest that a fluorine atom successfully stabilizes LC phases as long as dipole moment along molecular long axis is enough large.

References


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