Relationship Between Crystal Structure and Liquid Crystallinity of 1,1'-Disubstituted Ferrocene Derivatives

Takashi Okabe

Single crystal X-ray structure analysis of 1,1'-disubstituted ferrocene derivative, 1,1'-bis[ω-[4-(4-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]ferrocene (abbrevia- ted hereafter as bMAF-n, n=2〜12, where n is the number of carbon atoms in the methylene unit) has been carried out in this study. Crystal structures of bMAF-3, 5, 9 and 10 were determined, and relationship between molecular structure and liquid crystallinity of bMAF-n were discussed with the results of bMAF-2, 6 and 8. The molecular structure of bMAF-n is categorized into three groups by the location of the substituents. ①U-shaped structure ②S-shaped structure ③Z-shaped structure

The molecular structures of bMAF-3, 8, 9 and 10 adopted the U-shaped conformation in which the two substituents were located the same side with respect to ferrocenyl moiety. And the molecules formed a rod-like structure, which was favorable to show liquid crystallinity. On the contrary, the molecular structure of bMAF-5 was the S-shaped conformation in which the two substituents were present in the opposite directions, and the molecule formed the rod-like structure containing gauche conformation in methylene unit. The Z-shaped conformation was found out in bMAF-2 and 6, in which the substituents existed in opposite directions accompanying extremely bent structure at the flexible spacers. The rod-like molecular feature and high ratio of length to breadth ratio(aspect ratio) of the molecule are one of the most important points for bMAF-n to show liquid crystallinity.

The difference interaction networks were found out in crystals of U-shaped bMAF-n. In the crystals of bMAF-8, 9 and 10, which showed a monotropic-nematic phase and a smectic one, CH-π and π-π interactions existed in the neighboring molecules. On the other hand, bMAF-3, which showed only monotropic-nematic phase, had not only an intermolecular interaction but also an intramolecular interaction. Consequently, the difference may play an important role in giving rise to the mesomorphism.