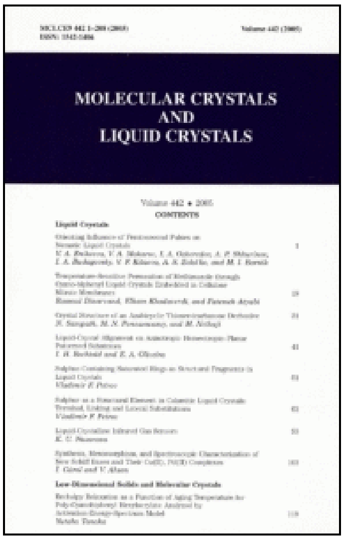

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Relationship Between Phase Transition and the Molecular Structure of Cholesteric Liquid Crystals

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The molecular rotation parameters of cholesteric liquid crystals (LCs) are calculated based on their phase transition temperatures using a semi-empirical molecular orbital method. A molecular rotation model is employed to evaluate the correlation between the LC phase transition and their molecular structure. The cholesteric-isotropic phase transition temperature and critical rotational velocity are regularly reduced with increasing molecular length. A novel explanation for the molecular interaction effect on phase transition is proposed. For low-temperature phases, the molecular interaction is strong and plays a key role in the phase transition. In contrast, for high-temperature phases, the molecular rotation effect becomes the important factor for the phase transition.

Keywords

Introduction

Cholesteric liquid crystals (LCs) exist universally in any organismic system. Studies on cholesteric LCs have shown their potential for application in cancer diagnosis and cardiovascular and circulatory system diseases [1]. The phase transition of cholesteric compounds plays a key role in its application not only as an LC material but also as a biomaterial.

LC phase characteristics can be effectively described by the mean field theory (MFT), which is based on molecular order parameters. The MFT deals with the approximate thermodynamic properties of an LC system. Several theories regarding phase transitions, including a famous theory proposed by Maier and Saupe [2], have been engendered based on MFT. However, few theories have aimed at investigating the mechanical or dynamical state of the LC system. In order to explain the phase behavior of some smectic LCs, Toriyama and Dunmur [3] advanced a mechanical rotational model of the LC system. Their model postulates that LC phases resemble micromachine systems that consist of an ensemble of molecular rotors. The

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mechanical rotational model of the LC system considers intermolecular forces, and such forces stimulate molecular rotations around the longest molecular axis.

From the mechanical rotational model point of view, molecules adopt different rotational motions for different thermotropic phases in order to accommodate different temperatures and energy environments. Generally, for high-temperature phases, the molecules rotate faster and more freely. When the molecular rotational speed reaches a critical level at some temperature, a mutation of the molecular order occurs, and the system undergoes a phase transition. As such, the mechanical model emphasizes that the state of molecular rotation determines the phase transition.

The thermal stability of phases and polymorphism are interpreted in terms of mechanics that involve basic parameters, such as the molecular center of gravity, moment of inertia, eccentricity, angular velocity, and mass deviation along the molecular axis [4]. In the some studies, the model was successfully applied to determine the thermal stability and characteristics of certain phases, such as the smectic, nematic, and multi-phases [5–10]. In one such study [6,8–10], Ma *et al.* investigated the conformational effects of inter-phenyl fluorinated LCs on the phase stability. While investigating the molecular rotational effects of heavy fluorine atoms substituted on the side of the molecular core, we found that isomeric LC molecules can take different shapes, which are referred to as *slim* and *fat* structures. For the twin molecules, we concluded that the slim isomer always exhibits better thermal stability than its counterpart fat isomer. This behavior is simply and quantitatively explained by mechanical parameters, such as the critical rotational velocity, moment of inertia, and eccentricity of the test molecules.

Molecular rotation around a long molecular axis has been observed in some studies, where the timescale was approximately 10^{-11} s [11–13]. Mitra *et al.* [13,14] investigated the molecular rotation of LC molecules with the quasi-elastic neutron scattering technique and provided a detailed rotational diagram. Their results indicated that the rotational motion of LC molecules determines their degree of order or mesophase behaviors.

Previous studies investigated a number of small molecules with high molecular velocity to determine the effects of molecular conformation on phase stability. In order to adequately support the validity of the above-mentioned model, more evidence is necessary, especially those involving larger molecules. In this study, a series of cholesteric LCs was chosen for studying the correlation between phase transition and crystal molecular structure. This was done by investigating parameters such as the moment of inertia, rotational velocity, and phase transition temperature.

Research Object

Figure 1 shows the molecular conformation of cholesteric LCs. We employed a series of cholesteric LC materials based on similar ring cores and side chains, where the spacer length, *n*, of alkyl side group, *R*, was from 0 to 13. The phase transition temperatures of the LCs are listed in Table 1, ordered by the spacer length, *n*, of the alkyl side group, *R*.

Computational Details

A semi-empirical molecular orbital method, called the *molecular orbital package* (MOPAC), was employed to evaluate the molecular parameters. Energy minimization and geometric optimization were adopted in the calculation procedure. The moment

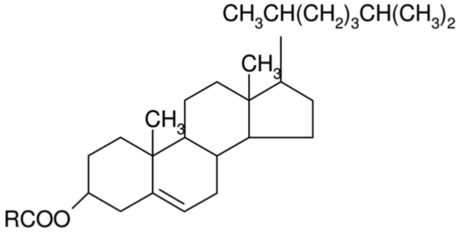

Figure 1. Studied molecular stucture of cholesteric liquid crystal compound.

of inertia was obtained from the calculation results, wherein the keywords were set as EF, AM1, PRECISE, and POLAR by the center-of-gravity coordinate system. The criterion for terminating all optimizations, both electronic and geometric, was an increase of 100 times (keyword PRECISE). Therefore, the precision of the moment of inertia computed by MOPAC was acceptable.

According to a general mechanical theory, a rigid molecular rotor always rotates around the longest principal axis of inertia because of its minimum moment of inertia. Therefore, we only discuss the molecular rotation around the longest principal axis. Furthermore, this research aimed to compare the mechanics parameters, so the molecules were considered to be independent, and their energy values were comprised of only the rotational kinetic energy. Thus, for a molecule at a certain temperature, an equipartition law was adopted to compute the rotational velocity. This energy could be described by the following equation [6,10]:

$$\frac{1}{2}kT_c = \frac{1}{2}I_A\omega_c^2 \tag{1}$$

Table 1. Phase structures and phase transition temperature T(K) of the series cholesteric LCs

n	Phase	T	Phase	T	Phase	T	Phase
0	Cr	370.65	Ch			(333.65)	I
1	Cr	389.65	Ch			(367.65)	I
2	Cr	368.35	Ch			384.95	I
3	Cr	375.15	Ch			386.15	I
4	Cr	366.15	Ch			374.65	I
5	Cr	372.65	Ch			374.65	I
6	Cr	387.15	SmA	(365.65)	Ch	(368.65)	I
7	Cr	383.15	SmA	(342.65)	Ch	(369.65)	I
8	Cr	353.65	SmA	(350.65)	Ch	365.15	I
9	Cr	358.65	SmA	(354.65)	Ch	365.65	I
10	Cr	365.65	SmA	(355.05)	Ch	(363.15)	I
11	Cr	365.15	SmA	354.65	Ch	(360.95)	I
12	Cr	336.65	SmA	351.95	Ch	(357.95)	I
13	Cr	344.55	SmA	352.45	Ch	(357.25)	I

where a rotor machine system with the moment of inertia I_A causes an inevitable criticality with a critical angular velocity at the transition temperature T_C. The equation relates the two important parameters ω_C and I_A, which represent the thermal stability characteristics of the LC molecular ensemble.

Results and Discussion

In the mechanical molecular rotation model of LC systems, we postulated that molecules assume rod-like shapes when they rapidly rotate around a long molecular axis. Therefore, the dynamic property of the molecular rotational state of the rotor is a key parameter for determining phase stability, particularly the phase transition temperature.

Figure 2 shows the correlation between the phase transition temperature and the moment of inertia of the molecules. Independent data regarding the moments of inertia and phase temperatures involve calculation results and measurement data, respectively. For Cr-SmA or Cr-Ch phases (i.e., the lower temperature melting phases), we are unable to find a regular correlation curve in the plot. This is likely due to the fact that intermolecular forces have the highest influence on the molecular rotational state at the crystal-smectic or crystal-cholesteric phase transitions. As we stated previously [9], the molecular rotational behavior of the Cr-SmA and Cr-Ch phases are different from that of the high-temperature Ch-I phase. In other words, the molecule is in non-free rotation. The influence of the mechanical properties on the molecular rotation is second only to molecular interactions.

For Ch-I phase transitions, a serrated picture for $n = 2-9$ and a regular linear correlation for $n = 9-13$ are shown in Fig. 2. This figure shows that the intermolecular forces in the Ch-I phase are weak and have little influence on molecular rotation. The rotational behavior of the molecules is free. Thus, the mechanical properties at this phase present a key influence in phase transition. The results are in agreement with the previous research conducted on the mechanical model [9,10].

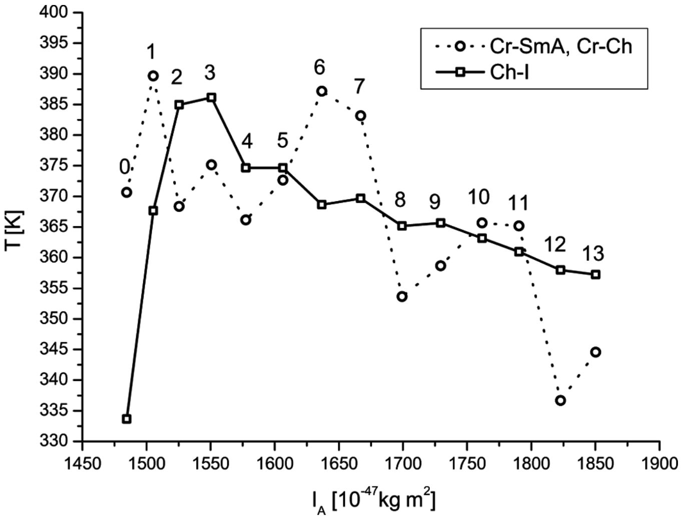

Figure 2. Correlation between Cr-SmA, Cr-Ch, and Ch-I phase transition temperature and moment of inertia of LCs. Near the circle symbols, the numbers express the spacer length *n* of the side alkyl *R*.

In the serrated curve of the Ch-I phase, the molecular structure symmetry displays an obvious odd–even pattern, except when $n = 0$, 1. This odd–even pattern in the LC phase transition temperatures has been widely reported in past literature [16–18]. In fact, several works have focused on the qualitative analysis of the molecular symmetry. Rarely, however, is a quantitative analysis reported.

In this work, we propose a quantitative parameter for the moment of inertia to express the molecular symmetry and rotational stability. The phase transition temperatures of $n = 3$, 5, 7, and 9 are slightly higher than those of $n = 2$, 4, 6, and 8. In the molecular long axis, the atomic mass distributions of odd n values are better than those of even n values. This indicates that molecular symmetry plays a role in the molecular rotation around a long axis. This, in turn, influences thermal phase stability. For the longer alkyl radical, where n is in excess of 9, the mass distribution balance between the right and left sides of the molecular core is thrown off. Thus, the molecular rotation around the long axis becomes unstable, resulting in a lower phase transition temperature. Because an increase of one alkyl radical brings negligible influences to the molecular symmetry, the odd–even effect disappears. When $n = 0$ or 1, the mass distributions between the two sides of the molecular core are in severe disequilibrium. As such, the molecular rotation and phase transition temperature for these are irregular compared with the other molecules.

Figure 3 shows the correlation between the Ch-I phase transition temperatures and the moments of inertia of a series cholesteric LCs, where n is divided into either odd or even. Except when $n = 0$ or 1, the correlation curves of I–T are smooth and regular. With increasing moment of inertia, the force of the molecular field experiences increasing difficulty in driving the molecule to rotate with rapid angular velocity (Fig. 4). The molecules have a small rotational inertia, which results in unstable rotations and lower phase transition temperatures.

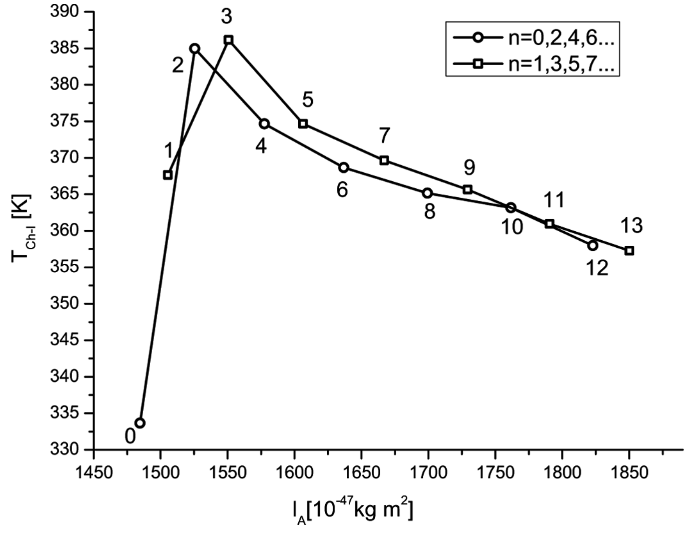

Figure 3. Ch-I phase transition temperature as a function of moment of inertia of the series cholesteric LCs. I–T data are divided into odd and even by the spacer length n of the side alkyl R. Near the symbols, the numbers express the spacer length n of the side alkyl R.

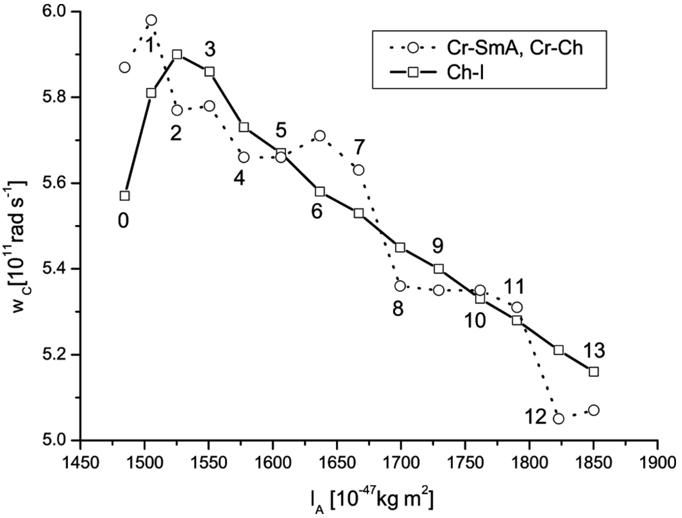

Figure 4. Correlation between the moment of inertia and the critical rotational velocity. Near the symbols, the numbers express the spacer length n of the side alkyl R.

Using Eq. (1), the critical angular velocity at the phase transition point can be computed. The correlation between the moment of inertia and the critical rotational angular velocity is illustrated in Fig. 4. Like the I–T relativity, the I–ω_c relative curves of the lower temperature phases, Cr-SmA and Cr-Ch, are irregular in shape. The molecular angular velocities are significantly disturbed by intermolecular forces. At the high-temperature phase, Ch-I, a smooth, regular, linearly decreasing function between the moment of inertia and angular velocity, is revealed, except when $n = 0$, 1. The larger the moment of inertia, the slower the angular velocity of the molecule is. As shown in Fig. 3, increasing the moment of inertia causes intermolecular forces to drive molecules to rotate more slowly. The slow molecular rotation and molecular order are easily disturbed. Hence, the thermal stability is poor and the transition phase temperature decreases.

On the other hand, also from Eq. (1), the moment of inertia has a conic inverse function with the angular velocity and not a linear correlation, providing that the phase transition temperature is fixed. From the measured phase transition temperature in our system, however, one can obtain a regular linear curve between the moment of inertia and the angular velocity. This can be used to forecast the phase transition temperature for a series of compounds by knowing the moment of inertia. This will be discussed more thoroughly in our next papers.

Conclusion

In view of the mechanical model of the LC system, the correlations between the moment of inertia, rotational angular velocity, and phase transition temperature of a series of cholesteric LCs were studied. The results suggest that the molecular structure, mass symmetry, and balance of the system are the chief factors that influence a molecular whirligig. Good molecular symmetry and balance are preferred for a stable molecular rotation. At their critical temperature points, compounds possess high phase transition temperatures. On the other hand, at low-temperature phases, intermolecular forces play strong roles and influence the system more, whereas molecular rotation effects influence the system less. At high-temperature phases, the molecular distance increases, and the interaction forces become weaker. In this phase, the transition temperature of the materials is strongly influenced by the state of molecular rotation. Finally, the linear curves between the moment of inertia and the angular velocity need to be more thoroughly investigated.

Acknowledgment

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