ORIGINAL PAPER

Rotational model for nematic phase stability of fluorinated phenylbicyclohexane liquid crystals

Heng Ma · Zhen-xin Li · De-heng Shi · Yu-fang Liu

Abstract A mechanical molecular rotation model for liquid crystal (LC) systems is employed to evaluate phase transition temperature of fluorinated phenylbicyclohexane isomeric LC compounds. Results show that when a fluorine atom is substituted along the molecular long axis, an LC molecule acquires high rotational speed and its rotation becomes stable, thereby resulting in a better thermal stability of the nematic phase. A novel explanation is proposed for the behavior of the nematic-isotropic phase of the LC system when a heavy atom is substituted along the molecular long axis.

Keywords Fluorine liquid crystal · Isomeric compound · Mechanical rotation model · Phase transition

Introduction

The mean field theory (MFT) is an approximation of the thermodynamic properties of a system; this theory is based on considering an order parameter to be spatially constant. It is a useful description if spatial fluctuations are not important. It becomes an exact theory only when the interactions in a system become infinite. In the last three decades, in several studies on phase transitions in materials, researchers have attempted to solve the phase transition problem by applying the MFT and have yielded several theories, such as the LC phase transition theory. The MFT can effectively explain several LC phases of materials; however, this theory cannot be applied to some important compounds, such as hydrogen isotope LC compounds. For several hydrogen isotope LC compounds [1], the MFT cannot effectively explain the difference in their phase transitions because of the same electron state in the molecules.

To study the effects of molecular interaction, most researchers investigating LCs always consider the electronic state of molecules previsionally. However, only few believe that the inter-molecular force acting between the electron clouds of neighboring molecules is related to the mechanical (dynamical) state of the molecules and not their electronic state. Therefore, few theories are aimed at investigating the mechanical or dynamical state of the LC system. A well-known theory by Maier and Saupe [2] emphasizes the assumption that the hard rod-like LC molecules are symmetric in structure although most of the molecules are asymmetric. This is because the LC molecules rotate around the molecular long axis. Therefore, an additional molecular freedom termed molecular rotational state, which is complementary to be MFT, should be introduced in the theory of the LC phase transition.

It is commonly known that most thermo tropic LC compounds have a characteristic geometric molecular shape -rod-like or lath-like-and each constituent molecule rotates rapidly around the molecular long axis [3]. In order to explain the phase behavior of some smectic LCs phase behavior, Toriyama and Dunmur [4] have proposed a

H. Ma (✉) · Y.-f. Liu
Department of Physics, Henan Normal University,
Xinxiang 453007, China
e-mail: hengma@henannu.edu.cn

Z.-x. Li
Department of Life Science and Technology,
Xinxiang Medical College,
Xinxiang 453003, China

D.-h. Shi
Department of Foundation,
The First Aeronautical College of Air Force,
Xinyang 464000, China

mechanical rotational model of the LC system. The model postulates that LC phases are micro machine systems consisting of an ensemble of molecular rotors. The model investigates the correlation between molecular rotation and molecular conformation in order to characterize the mesogenic properties of LC systems.

The mechanical rotational model of the LC system considers the intermolecular forces (forces between the electrons of a molecule and the others of the neighboring molecule), and such forces stimulate molecular rotations around the longest molecular axis. The phenomena of the thermal stability of phases and polymorphism are interpreted in terms of mechanics that involving basic parameters such as molecular center of gravity, moment of inertia (I_A), eccentricity (ε), angular velocity (ω_c), and mass deviation along the molecular axis (δ) [5]. In previous studies, this model has been successfully applied to explain the thermal stability and characteristics of phases such as the smectic phase, nematic phase, and multiphase's [4–8].

In LC system, molecules adopt different rotational motions for different thermotropic LC phase. For the smectic phase, the molecules rotate in a limited space. With increasing temperature, the system obtains sufficient energy and the molecules rotate more speedy and freely around the long molecular axis. As the molecules rotate at a determinate level at a critical temperature, the system undergoes a phase transition. Thus, the mechanical model emphasizes that the molecular rotation state determines the phase transition in the LC system.

Mitra et al. have studied the rotational motions of LC molecules by means of the quasi-elastic neutron scattering technique and provided a detailed diagram of molecular rotation [9, 10]. Furthermore, experimental investigations have provided some accurate time scales of the molecular rotation frequency [10–12]. The obtained results indicate that the rotational motions determine the degrees of the order of the LC molecules, i.e., mesophase behaviors.

In the previous studies [6, 13], Ma et al. have studied the conformational effect on the phase stability in terphenyl fluorinated LCs. By investigating the molecular rotational effect of heavy fluorine atoms substituted on the side of the molecular core, we find that isomeric LC molecules take different shapes, which are called "slim" and "fat" structural phenomena. For the twin molecules, we concluded that the "slim isomer" always exhibits better thermal stability than its isomeric counterpart, the "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 considered molecules.

In a recent study [13], the validity of the mechanical model has been clarified theoretically. The study affirms that the positional difference of a heavy atom substituted in isomeric molecules adversely affects the mechanics of molecular nuclei-frame and therefore affects the molecular rotational state. The essential characters of thermotropic LC exist in their unique rotational state around the longest molecular axis which has minimal moment of inertia.

In order to adequately prove the validity of the above mentioned model, it is necessary to relate some known experimental parameter (e.g., phase transition temperature) with some unknown parameters that can be calculated conveniently. In this study, the authors have selected several isomeric phenylbicyclohexane (PBC) LC molecules in which the fluorine atoms are substituted on the terminal of the molecular long axis, in order to investigate the effect of heavy atoms on the crystal-nematic (CrN), smectic-nematic (SmN), (which is called by a joint sign XN) and nematic-isotropic (NI) phase behaviors. The study is aimed at presenting a simple and effective method for forecasting the LC phase behavior during the design of new materials.

Method and studied target

Generally, a rigid molecular rotor always rotates around the longest principal inertia axis because of the minimum moment of inertia of the rotor. The moment of inertia is inherent to a molecule and is determined by the atomic mass distribution. In this model, we postulate that the LC molecules rotate around only the longest principal axis; a heat bath is used for the correspondence between the thermodynamic system and its classical mechanical correspondence in the machine system. Because the study aims to compare the mechanical parameters of structural isomers, the molecules are considered to be independent, and their energy comprises only the kinetic energy required for the molecular rotation. Thus, for a single molecule at a definite time or temperature point, the equipartition law is expressed by the following equation [6, 13]:

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

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.

The explanation of the rotational velocity of LC molecules is reliable because a rotational velocity similar to that explained above has been observed in some experiments on LC compounds. The time scale is approximately $10^{-11}\sim10^{-10}$ s [10–12]. In this study, the moment of inertia is a key parameter which should be provided in a precise manner. On the other hand, our investigation is

implemented in a comparative method for isomeric molecular groups, so it is important to ensure the molecular calculation in a same test conditions. Over the years, various molecular calculation methods have been developed, the semiempirical method is more accurate than empirical methods less accurate than ab initio methods. Therefore, a semiempirical molecular orbital method termed molecular orbital package (MOPAC) is employed in our calculations, which a congener phenylbicyclohexane molecular core is used. And energy minimization and geometric optimization are adopted in the MOPAC. The moment of inertia can be obtained from the molecular calculation, in which the keywords are set as EF, AM1, PRECISE, and POLAR by the center-of-gravity coordinates system. The criteria for terminating all optimizations, electronic and geometric, are to be increased by 100 times (keyword PRECISE). Therefore, the precision of the moment of inertia computed by MOPAC is acceptable.

From the moment of inertia and phase transition temperature of the LC compounds, the critical velocity ω_c can be determined using Equation 1. The phase transition temperatures are obtained from the database [14] of liquid crystalline compounds. The target molecular configuration is shown in Fig. 1, and the NI phase transition temperature, calculated moment of inertia, and critical velocity are listed in Table 1.

The compounds shown in Table 1 are divided into six groups on the basis of the length of terminal alkyl radicals. The phase properties and mechanical parameters of the isomeric molecules having different substituted positions of the fluorine atoms are compared.

Results and discussion

NI phase transition temperature and fluorinated effect

From Table 1, we first analyze the moment of inertia of the isomeric molecules. Except for the group 2pbc series, every group has at least one isomeric molecular object comparing two or three molecules. By comparing the moments of inertia listed in this table, it is obvious that the position at
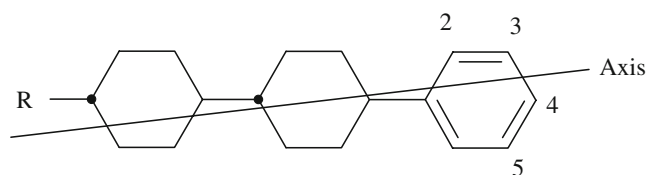
Fig. 1 Molecular conformation of fluorinated bicyclohexylphenyl compounds. $R = C_nH_{2n+1}$, $n = 2 \sim 7$. The fluorine atoms are substituted in different positions 2, 3, 4, and 5 of the phenyl ring, respectively. The axis expresses molecular long rotation axis

which the fluorine atom is substituted strongly influences the value of the moment of inertia. One can obtain a relationship order between the fluorine positions and the moments of inertia as follows:

$$I_A(4) < I_A(3) < I_A(2); \quad I_A(34) < I_A(24) < I_A(23)$$
$$< I_A(35); \quad I_A(234) < I_A(345).$$

where, the numbers in the brackets denote the positions of the fluorine atoms substituted on the phenyl ring (see Fig. 1).

In view of the mechanical model, if the rotation of molecular rotors is stable, LCs that comprises the rotors possess good thermal stability, i.e., the LC compound possesses a high phase transition temperature. In our calculation of the *n-PBC* compounds (where no fluorine atom is substituted), we find that the long molecular rotation axis passes through the line connecting positions 3 and 4; however, it is closer to position 4 than to position 3. As a result, the fluorine atom substituted at position 4 is near the long molecular rotation axis; however, the fluorine atoms at positions 2, 3, and 5 are far from the long molecular rotation axis. The molecule whose fluorine atom is substituted at position 4 is slim; the molecules whose fluorine atoms are substituted at the other positions are fat.

Because of the contribution of the fluorine atoms to the I_A, it is reasonable that the moment of inertia of fat molecules is larger than that of slim molecules. In other words, the PBC LC compounds with terminal fluorine substitution also exhibit the slim-fat phenomenon observed in the terphenyl LC compounds with side fluorine substitution, investigated in our previous studies. Thus, the mechanical model can be applied to not only side radical substitution but also terminal radical substitution.

We have also found that the NI transition temperature and not the XN transition temperature is strongly influenced by the fluorine atoms substituted at position 4. Figure 2 shows the temperature distribution of the NI phase transition of the compounds. The phase transition temperatures are arranged in ascending order. It is interesting to note that all the compounds of the npbc4f group are distributed over the high-temperature area (> 415K), and the compounds of the npbc24f2, npbc34f2, and npbc234f3 groups are distributed in the temperature range 385K-400K. For the other compounds, i.e., those of the npbc2f and npbc3f groups and compounds correlated to the position of the fluorine atom at 23, 35, and 345, the temperatures are distributed over the lower-temperature area (< 375K). This clearly indicates that position 4 of the phenyl ring is an important position for the NI phase transition temperature of LC compounds.

The regular temperature distributions suggest that the molecular conformation, the molecular rotation, and the NI phase transition retain a close correlation. It is believed that

Table 1 Studied LC compounds, CrN or SmN (XN), NI transition temperature (K), moment of inertia (10^{-47}kg·m^2), and critical velocity (10^{11}rad/s)
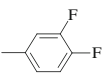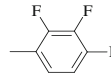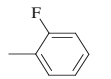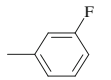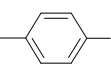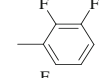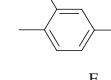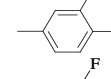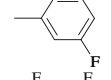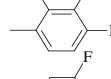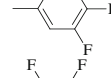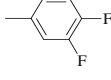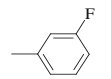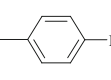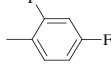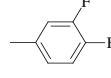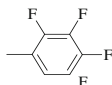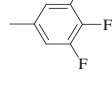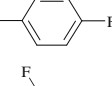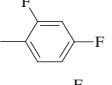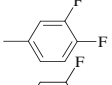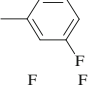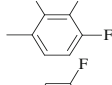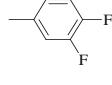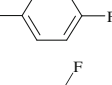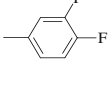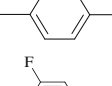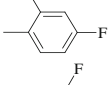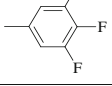
Compounds	F atoms on phenyl ring	I_A	T_{XN}	ω_{cXN}	T_{NI}	ω_{cNI}
2pbc34f2		715	325.0	7.92	358.6	8.32
2pbc234f3		877	321.8	7.12	353.6	7.46
3pbc		613	365.0	9.06	373.6	9.17
3pbc2f		845	321.6	7.25	352.4	7.59
3pbc3f		786	329.7	7.61	365.4	8.01
3pbc4f		687	361.8	8.53	431.7	9.31
3pbc23f2		920	354.2	7.29	369.6	7.45
3pbc24f2		874	343.2	7.36	399.2	7.94
3pbc34f2		814	318.2	7.34	397.4	8.21
3pbc35f2		1013	324.1	6.64	360.8	7.01
3pbc234f3		968	310.6	6.65	390.0	7.46
3pbc345f3		1025	338.1	6.75	367.0	7.03
3pbc2345f4		1219	337.2	6.18	366.2	6.44
4pbc3f		873	338.2	7.31	361.2	7.56
4pbc4f		790	353.8	7.86	425.2	8.62
4pbc24f2		972	319.2	6.73	398.2	7.52
4pbc34f2		910	313.7	6.90	391.5	7.70

Table 1 (continued)

Compounds	F atoms on phenyl ring	I_A	T_{XN}	ω_{cXN}	T_{NI}	ω_{cNI}
4pbc234f3		985	314.8	6.64	391.5	7.41
4pbc345f3		1132	339.4	6.43	364.3	6.66
5pbc		802	382.2	8.11	383.2	8.12
5pbc3f		908	348.2	7.28	363.2	7.43
5pbc4f		835	348.7	7.59	430.7	8.44
5pbc24f2		1014	346.1	**6.86**	**394.2**	**7.32**
5pbc34f2		952	320.2	6.81	400.2	7.62
5pbc35f2		1158	308.2	6.06	367.4	6.62
5pbc234f3		1101	314.9	6.28	395.7	7.04
5pbc345f3		1182	360.5	6.49	374.4	6.61
6pbc3f		1015	353.2	**6.93**	**367.7**	**7.07**
6pbc4f		962	356.9	7.15	418.9	7.75
6pbc34f2		1073	327.6	6.49	389.2	7.08
7pbc3f		1056	348.7	6.75	372.8	6.98
7pbc4f		1016	339.1	6.79	415.2	7.51
7pbc24f2		1184	344.2	6.33	387.2	6.72
7pbc345f3		1377	341.7	5.85	371.0	6.10

Positions and numbers of the substituted fluorine atoms are indicated by a phenyl ring
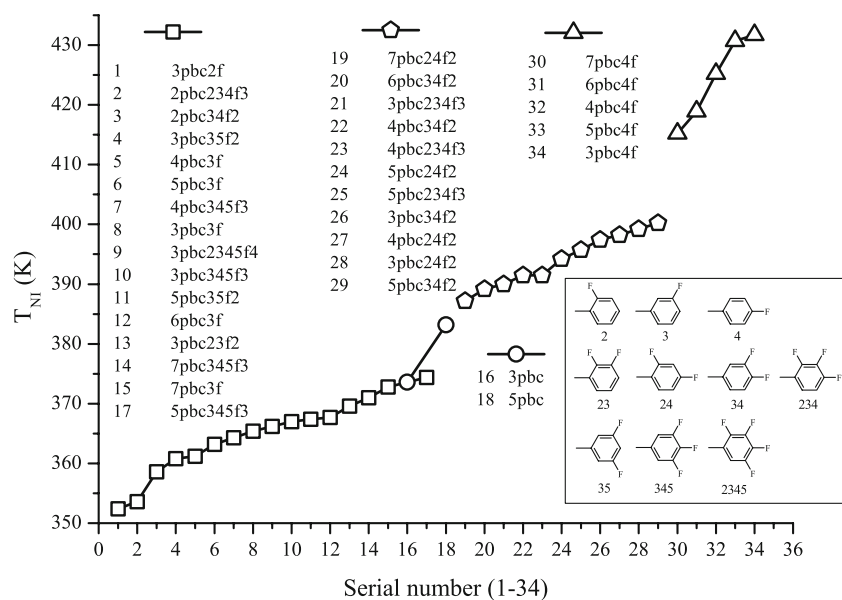
Fig. 2 NI phase transition temperature distribution. The phase transition temperatures are arranged in ascending order. The horizontal coordinates express the serial number of the compounds listed in the Figure. The block schematic diagram indicates the position of the substituted fluorine atoms at the phenyl ring

slim molecules rotate stably and always exhibit better thermal stability than their isomeric counterparts, i.e., fat molecules. The temperature distribution characteristics have proved that the concept and model of the slim-fat phenomenon are valid for both the side fluorine substitution and the terminal fluorine substitution. The results show that fluorine atoms substituted along the molecular long axis play an important role in determining the NI phase transition.

Molecular rotation for NI phase transition

The correlation between the moment of inertia and critical rotation velocity is shown in Fig. 3. For all groups, there exists a negative correlation among the molecules, i.e., a small moment of inertia and high rotational velocity. It is necessary to clarify that the negative correlations are obtained from the different I_A $_-\omega_c$ data of different molecular isomeric groups and not from Equation 1. For every isomeric group, although different molecules have different moments of inertia (calculated data) and different NI phase transition temperatures (experimental data), slim isomers and fat isomers always exhibit contrasting characteristics with regard to the mechanical parameters. As a result, the speed at which a slim isomer with a small moment of inertia can rotate around the molecular long axis is higher than that of the fat isomer.

By analyzing the ω_c and the NI transition temperatures, a positive correlation is obtained, as shown in Fig. 4. The slim isomer, which possesses higher velocity, has a higher transition temperature than that of the fat isomer. In view of

the mechanical model, the slim isomeric molecule rotates at a higher speed than its counterpart does; therefore, the motion of the slim molecule is highly stable, i.e., its phase transition temperature is high.

Two pairs of groups are exceptions to the above behavior 3pbc34f2 and 3pbc24f2, 4pbc34f2 and 4pbc24f2, shown in Fig. 4 (also see Fig. 5). The reason for this exception may the dynamic impedance matching [5] between the terminal alkyl unit and intermolecular fluorine atoms. In the nematic phase, the impedance matching among the subunits in a molecule is important. For groups 3pbc24f2 and 4pbc24f2, it is possible that the positional relationships among the propyl radicals, butyl radicals, and fluorine atoms result in good dynamic impedance matching to the rotation motion. To confirm this, a more quantitative analysis is required. A comprehensive investigation and explanation of this case will be presented in a future study.

Figure 5 illustrates the moment of inertia as a function of the NI phase temperature. The moment of inertia and the NI phase temperature are independent calculation data and experimental data, respectively. A graphical representation of the data of the isomeric molecules reveals that the two parameters exhibit an inverse relationship, i. e., the slim isomer that has a small moment of inertia possesses a higher phase transition temperature than that of the fat isomer. A slim molecular shape implies that the molecule has a slight chance of colliding with other molecules; further, the small moment of inertia causes the rotation of the molecule to be stable. Therefore, the rotational stability of the slim isomer is higher than that of the fat isomer.
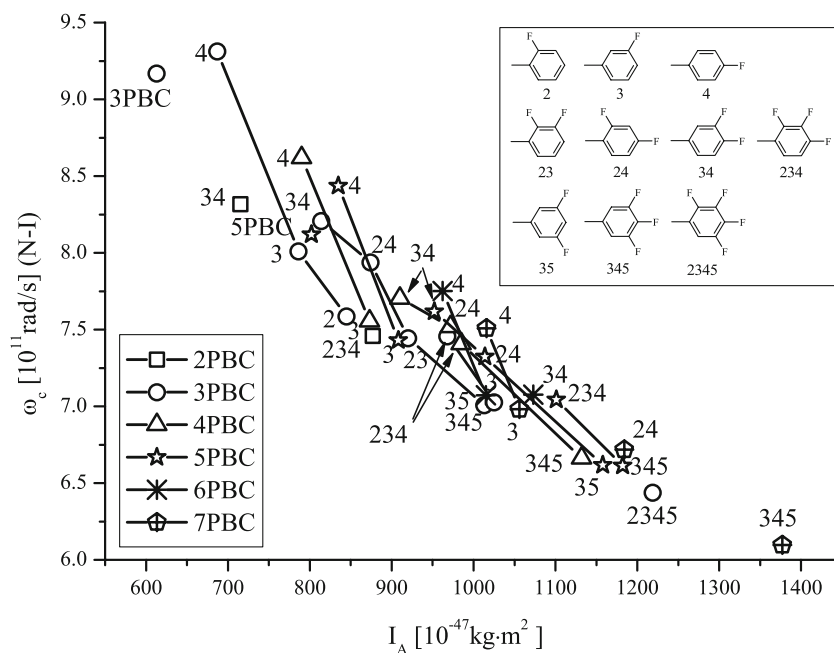
Fig. 3 Correlation between moment of inertia and critical velocity (NI phase transition) obtained from Equation 1. A continuous line is used to connect the symbols of isomeric group molecules. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at phenyl ring. The positions of the fluorine atoms are also pictured in a block schematic diagram

Molecular rotation for XN phase transition

From the viewpoint of the mechanical model, the LC molecules undergoing the NI phase transition have a weak interaction and low potential and can rotate freely; therefore, the molecular rotation plays a key role. In low-temperature phases, such as the CrN and SmN phases, the rotation of the molecules is limited in a fixed space. The molecules have distinct external and internal interaction potentials, which strongly affect the phase transition temperature. For the XN phase transition, the correlations of the data of the transition temperature, critical angular
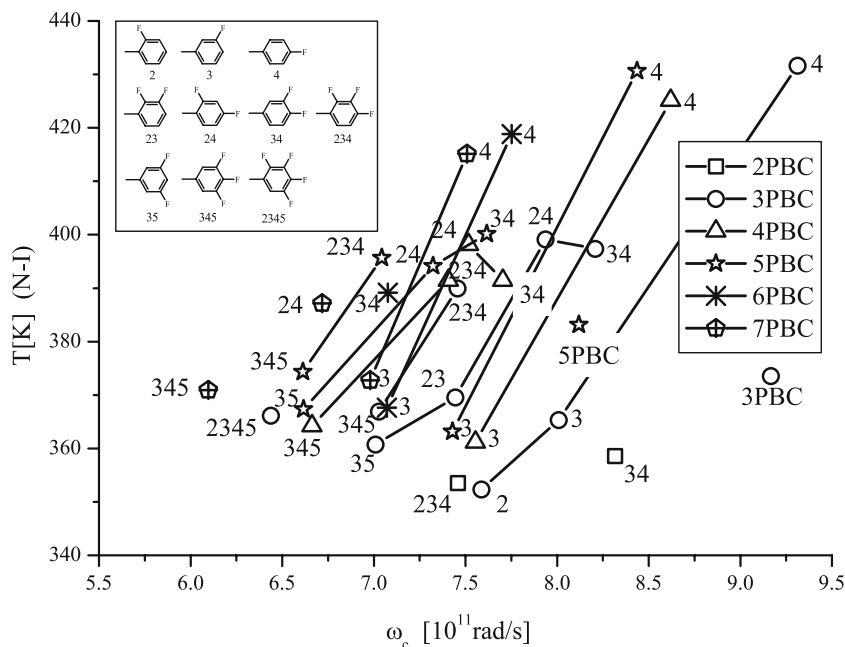

Fig. 4 Corresponding to NI phase transition, temperatures are shown as a function of critical velocities. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at phenyl ring. The positions of the fluorine atoms are also pictured in a block schematic diagram
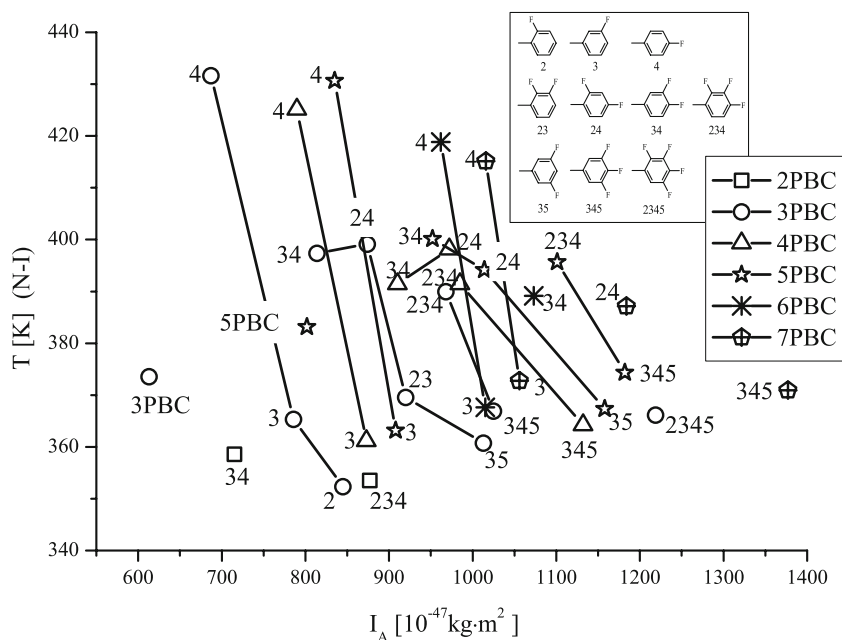
Fig. 5 Correlation between NI phase transition temperature and moment of inertia of the isomeric compounds. The moment of inertia and the NI phase temperature are independent calculation data and experimental data, respectively. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at the phenyl ring. The positions of the fluorine atoms are pictured in a block schematic diagram

velocity, and moment of inertia are in clutter state, which hints that the XN phase is out of the scope of the mechanical model. Figures 6, 7, and 8 show the relationship among the phase transition temperature, critical angular velocity, and moment of inertia for the XN phase transition.

By comparing Figs. 3 and 6, 4 and 7, and 5 and 8, we can observe that the isomeric-group data shown in Figs. 3, 4, and 5 (NI phase transition) show a good correlation; however, the isomeric-group data shown in Figs. 6, 7, and 8 are not well correlated. The main reason for this is that
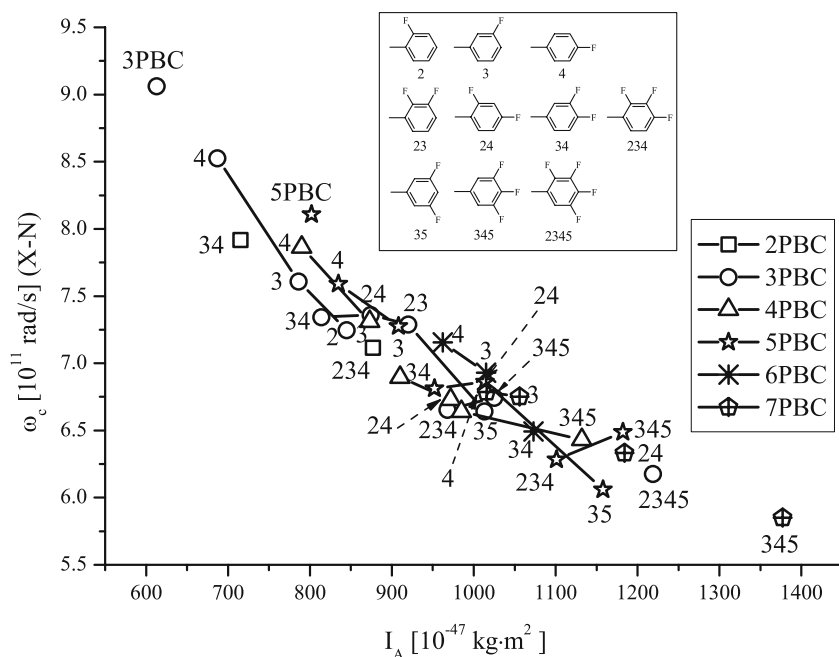

Fig. 6 Correlation between moment of inertia and critical velocity (XN phase transition) obtained from Equation 1. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at the phenyl ring. The positions of the fluorine atoms are pictured in a block schematic diagram

Fig. 7 Corresponding to XN phase transition, temperatures are shown as a function of critical velocities. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at the phenyl ring. The positions of the fluorine atoms are pictured in a block schematic diagram
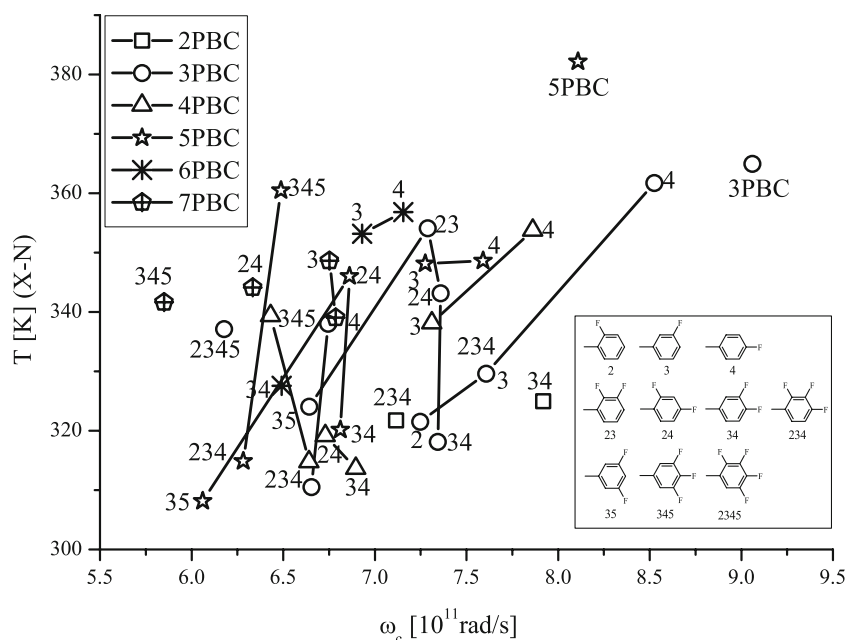
the external and internal molecular forces have the highest influence on the molecular rotation for the crystal-smectic or crystal-isotropic phase transition point, and the influence of the mechanical properties is secondary. As mentioned previously, the molecules take different shapes at the XN

and NI phase transition points. The obtained results are in agreement with the findings of the previous studies on the mechanical model [8]. Therefore, the mechanical rotation behavior can be effectively explained and described by the mechanical model.
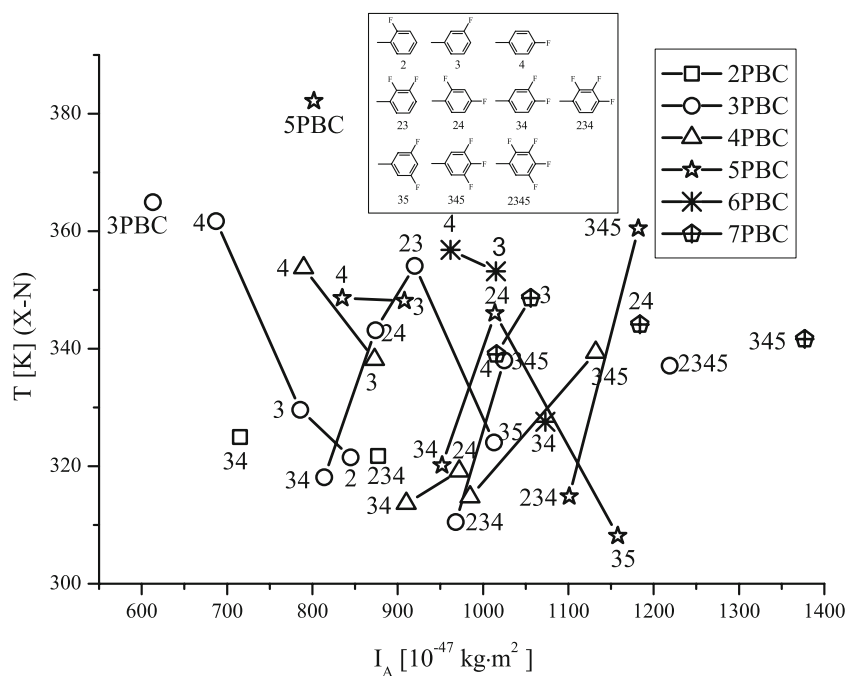

Fig. 8 Correlation between XN phase transition temperature and moment of inertia of the isomeric compounds. The moment of inertia and the phase temperature are independent calculation data and experimental data, respectively. Near the symbols, the numbers express positions and numbers of the fluorine atoms substituted at the phenyl ring. The positions of the fluorine atoms are pictured in a block schematic diagram

Conclusions

In view of the mechanical model of the LC system, the effect of fluorine atoms substituted in PBC core has been studied. Fluorine atoms substituted at the terminal of the molecular core cause the LC molecules to be slim and fat, respectively. The results suggest that a heavy fluorine atom substituted at the terminal of the molecule strongly influences the molecular rotational state, furthermore, determines the thermal stability of the NI phase. The study provides new evidences for the phase transition behaviors of an LC system and expands the application of the mechanical rotation model of the LC system.

This investigation has provided not only a reasonable explanation of the correlation among the NI phase transition, molecular rotation velocity, and moment of inertia, but also useful information on a new molecular design obtainable by a simulation method. Therefore, an application of the mechanical rotational model, of which the discussion of slim-fat molecular shape can be useful for forecasting the LC phase behavior before synthesis of new LC materials, is expected.

However, the mechanical model of the LC system cannot calculate the precise phase transition temperature; it can only forecast the trend of the transition temperature among isomeric LC compounds.

References

1. Neubert E (1985) Mol Cryst Liq Cryst 129:327–374
2. Maier W, Saupe A (1960) Z Naturforsch 15a:287–292
3. Gasch R, Pfuytzner H (1975) Rotordynamik Einefuhrung. Springer, Berlin
4. Toriyama K, Dunmur DA (1993) Liq Cryst 13:797–810
5. Xu J, Okada H, Onnagawa H, Sugimori S, Toriyama K (2000) Jpn J Appl Phys 39:1801–1807
6. Ma H, Xu J, Okada H, Sugimori S, Onnagawa H, Toriyama K (2004) Jpn J Appl Phys 43:1481–1487
7. Toriyama K, Kimura H, Onnagawa H (2001) Jpn J Appl Phys 40:5000–5007
8. Ma H, Sun RZ, Li ZX (2006) Chin Phys 15:1009–1014
9. Mitra S, Venu K, Tsukushi I, Ikeda S, Mukhopadhyay R (2004) Phys Rev E 69:061709(8)
10. Mitra S, Mukhopadhyay R, Venu K (2000) Chem Phys 261:149–156
11. Richardson RM, Leadbetter AJ, Frost JC (1982) Mol Phys 45:1163–1191
12. Mitra S, Sastry VSS, Venu K, Mukhopadhyay R (2005) Chem Phys Lett 406:263–267
13. Ma H, Xu J, Onnagawa H, Okada H, Sugimori S, Toriyama K (2007) Jpn J Appl Phys 46:293–298
14. Volkmar V (2002) Database of liquid crystalline compounds Ver. 4.1. LCI , Hamburg, Germany