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MECHANICAL ROTOR-BEARING MODEL FOR LIQUID CRYSTAL SYSTEMS

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Mechanical Rotor-Bearing Model for Liquid Crystal Systems

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The liquid crystal phases are postulated as a mechanical rotor-bearing system in which liquid crystal molecular core and terminals are estimated as the rotor and axes, respectively, the terminals also function as molecular rotors in the subsequent layers. Some general rules are proposed that relate phase stability to molecular structures and the mechanical rotor-bearing model is applied to explain the phase behaviors. Phenomena of the thermal stability of phase and phase transition are explained in terms of basic mechanical and dynamical parameters: center of gravity, eccentricity, moment of inertia and mass distribution. Fluorination effects on liquid crystallinity are explained in a uniform manner by mechanical and dynamical basis. Moreover, we have also examined interesting liquid crystalline systems such as liquid crystal oligomers. Characteristic thermal behaviors are correlated to the molecular structures and their mechanical or dynamical parameters to complete validity of the model proposed.

Keywords: liquid crystal; moment of inertia; thermal stability; rotor-bearing model

INTRODUCTION

It is well known that Liquid crystal (LC) molecules almost have elongated shape. In liquid crystalline phases, the molecules are parallel to each other with their principal axes, and form various anisotropic phases. They also rotate rapidly around their principal axes [1].

For mechanical LC model, a simple example has been applied to Smectic B phase by one of the authors [2]. The thermal stability and the phase transition to higher temperature phases are modeled and successfully explained by the theory of critical point in mechanical engineering [3,4].

In this paper a mechanical model, rotor-bearing model, is applied to examine the thermal stability and the phase behaviors of terphenyl and fluorinated terphenyl liquid crystals. We consider the mechanical systems in which liquid crystalline molecules are rapidly rotating as parts of ensemble of molecular rotors. As a rotor, molecule is changeable or adjustable in its shape according to the environmental conditions, e.g., it possesses potential for organization of an optimum shape through its conformational changes in given circumstances. Such transformation in shape also induces the characteristics of the mechanical system itself. The concept of mechanics and dynamics: distribution of mass, moment of inertia, location of center of gravity in the core rotor, is quantitatively or qualitatively (in case of difficulty in quantitative treatment) analyzed.

LC MOLECULAR STRUCTURES

The molecules studied in this paper are listed in Figures 1 and 2. The symbol for the molecular structures are exemplified as follows: for symbols 5.rFF.O8, the 5, O8 means the $-C_5H_{11}$, $-OC_8H_{17}$ terminal

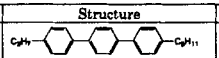
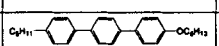
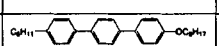
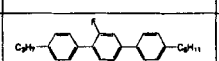
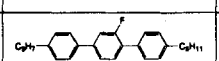
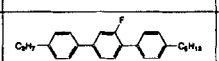
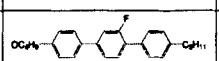
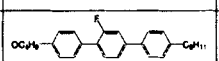
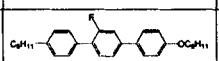
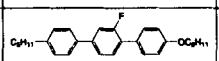
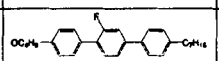
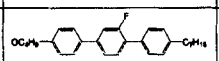
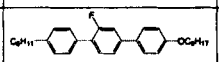
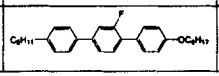
No.	Symbol	Structure	Trans. Temperature (°C)
1	3.5		Cr:180.0E:200.0B:214.0A:218.0 [5]
2	5.O6		Cr:205.0B:216.0A:228.5 [6]
3	5.O8		Cr:194.5B:211.0A:221.5 [6]
4	3.clF.5		Cr:55.0B:61.0A:99.5N:141.5 [7]
5	3.crF.5		(20.0)Cr:50.0(C:13.0A:16.0)N:140.6 [7]
6	3.crF.6		Cr':39.0Cr:44.5(B:37.5C:42.0)A:71.5 N:132.0 [5]
7	4O.crF.5		Cr:59.5E:85.5B:86.5C:99.5A:144.0 N:176.0 [6]
8	4O.clF.5		Cr:65.5C:96.5N:172.5 [6]
9	5.clF.O6		Cr:70.0G:78.0B:92.0I:93.0C:118.0 A:155.0N:166.5 [6]
10	5.crF.O6		Cr:62.5J:47.5(I:50.0)C:113.5N:162.5 [6]
11	4O.clF.7		Cr:50.0B:88.8C:107.7A:135.9N:161.7 [6]
12	4O.crF.7		Cr:67.5E:79.2B:87.0A:148.0N:166.4 [6]
13	5.clF.O8		Cr:69.0G:83.0B:100.5C:124.0A:158.0 N:161.0 [6]
14	5.crF.O8		Cr:47.0J:40.0I:53.5C:116.5A:130.0 N:155.0 [6]

FIGURE 1 Structures of terphenyls and their fluorinated derivatives.

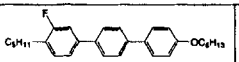
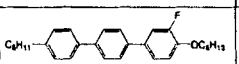
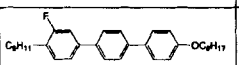
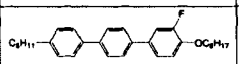
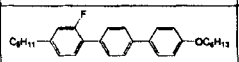
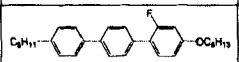
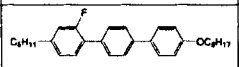
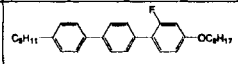
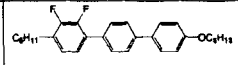
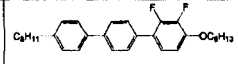
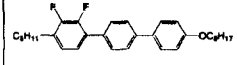
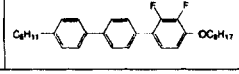
15	5.llF.O6		Cr:?G:176.0A:210.0 [6]
16	5.rrF.O6		Cr:?G:160.0C:162.0A:201.0 [6]
17	5.llF.O8		Cr:?G:170.5C:176.5A:202.5 [6]
18	5.rrF.O8		Cr:?G:146.0B:158.0A:195.0 [6]
19	5.lrF.O6		Cr:115.0C:131.5N:166.5 [6]
20	5.rlF.O6		Cr:83.5(K:48.5J:62.0)C:105.0 N:166.0 [6]
21	5.lrF.O8		Cr:102.0(I:99.5)C:137.5N:160.0 [6]
22	5.rlF.O8		Cr:69.0(K:25.0J:43.5)C:119.0 N:158.0 [6]
23	5.lFF.O6		Cr:101.5C:156.5A:167.0N:171.5 [9]
24	5.rFF.O6		Cr:97.5C:145.5N:166.0 [9]
25	5.lFF.O8		Cr:89.0C:155.5A:165.0N:166.0 [10]
26	5.rFF.O8		Cr:93.5C:144.0A:148.0N:159.0 [11]

FIGURE 1 Continued.

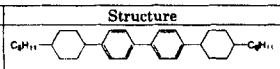
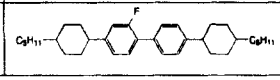
No.	Symbol	Structure	Trans. Temperature (°C)
27	5.CBC.5		Cr':43.0Cr':45.0Cr:55.0B:247.0 A:275.0N:305.0 [10]
28	5.C.lrF.BC.5		Cr:80.0S1:156.0S2:181.0 N:278.0 [13]

FIGURE 2 Structures of cyclohexylbiphenylcyclohexane and its fluorinated derivatives.

groups, respectively. The rFF means that the phenyl ring at right side possesses two fluorine atoms side by side. The lowercase letter r is abbreviation of "right". Similarly, l means left and c means center. In the same way, the crF means that the right position on central phenyl ring possesses one fluorine atom.

RESULTS AND DISCUSSION

The fundamental mechanical and dynamical parameters, i.e., center of gravity, eccentricity, mass distribution and moment of inertia, are calculated using a semiempirical molecular orbital package (MOPAC).

Phases and Sequential Phase Behaviors of the LC System on Mechanical and Dynamical viewpoint

From a dynamic viewpoint, the composition of the considered liquid crystalline system that consists of rigid core and flexible terminal groups should induce clear mechanical and dynamical characteristics of each part of the molecule. Interestingly, with such simplicity in structure of the system, we can classify these phases in three groups: ordered smectic phase or crystalline phase (SmE, SmK, SmG, SmJ, SmB, SmI), less ordered or high temperature smectic phase (SmC, SmA) and nematic phase. The ordered smectic phase will be well modeled by the rotor-bearing model as already demonstrated in the previous paper [2]. Less ordered smectic phases (SmC, SmA) could be assigned to partially degraded rotor-bearings ensemble systems. Increase of conformational freedom in the terminal axes of alkyl or alkoxy chains in higher temperature region, induces less ordered bearings structure that produces ineffective functions at the layer-interfaces. Molecular rotor in the nematic phase is almost a free-rotor suspended in an uniaxial potential field.

Eccentricity ε and Deviation δ

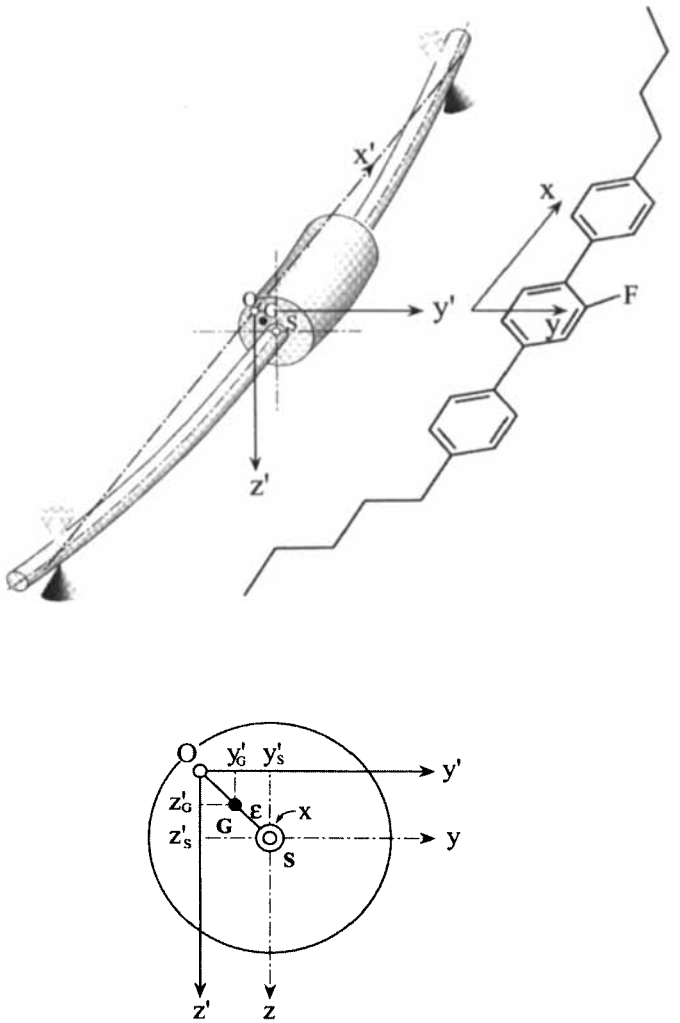


FIGURE 3 Cartesian coordinates fixed at a liquid crystalline molecule in a bent conformation.

The ordered phases (SmE, SmK, SmG, SmJ, SmB, SmI) for which the rotor-bearings model is valid [2], are concerned with the effect of the relative location between the center of gravity and geometrical center of the core on dynamics of the mechanical systems.

To analyze effects of displacement of the center of gravity from the geometrical center of the core, a Cartesian coordinates system (x, y, z) fixed on the molecule, is adopted for the calculation of mechanical parameters such as eccentricity and moment of inertia. The x-axis is taken in the direction of rotational axis of the rotor. The other two axes are in the plane perpendicular to the molecular long axis (see Figure 3).

In an ideal rotor-bearing system, the center of rotor S is on the line that connects the two bearings. Some deviation of S from the origin O on that line will be inevitable. The deviation of the center of gravity G from the center of rotor S, can be consist of two major quantities: one is a deviation within the yz-plane, and the other is a deviation within the xy-plane. The former is so called eccentricity ε. We call the latter as the deviation δ or more clearly δ_{XY} in this paper. The two parameters: ε and δ are not constant but change themselves associate with change in the molecular conformations.

For example, in low temperature crystal phases such as SmB, terminal chains are confined in hexagonal array lattice to stretch parallel to the rotational axis. Possible trans and gauche conformational manifolds in each $-CH_2-CH_2-$ bond site in the terminals and the flexibility of the aliphatic-chains will allow dynamical changes time to time but also result in time-averaged form of an elongated conformation parallel to the rotational axis. In this system, points O, S and G are coincide. This structure will correspond to a rigid rotor and bearing model [2,4]. If a molecular system has a potentiality for elasticity in its long axis, it should be modeled by elastic rotor and bearing model [2,4].

Less ordered phases such as SmC and SmA may have more freedom to take splayed of bent conformational forms in the molecule.

An example of molecular conformational form: a bent form is illustrated in Figure 3 and modeled an elastic rotor and bearing system with bent axis.

Ordered phases

The effect of eccentricity in dynamics appears as centrifugal force on the center of gravity G. A centrifugal force acting on a rigid rotor is given by $\varepsilon m\omega^2$. In an elastic rotor and bearing, the rotor feels centrifugal force: $m(\rho_\varepsilon + \varepsilon)\omega^2$ in rotation with rotational speed ω, where ρ_ε is deviation of S from point O that originate in elasticity of the axis (see Figure 3). An estimation or evaluation of ρ_ε is extremely difficult. If it is assumed that values of ρ_ε are same in comparison of similar molecular systems, one can analyze the contribution of the eccentricity comparatively within the systems.

Molecules consist of rigid core and short terminal chains will be well modeled by the rigid-rotor and bearing model. The potentiality of bent in terminal chains will allow molecular bent form shown in Figure 3. The 4,4"-dipentyl-cyclohexylbiphenylcyclohexane (5.CBC.5) should be modeled by elastic rotor.

In ordered phases it is requested a parallel conformations of terminal chains to the core, that means the center of rotor S is nearly on the line that connects the two bearings.

A deviation of G along x-axis will be introduced by disproportion of terminal chain length. The effect of deviation δ is less significant for the ordered phase stability. It is concluded that the effect of eccentricity ε is vital for stability of ordered phases.

Fluorination also accompanies deviation δ: a deviation within the xy-plane. One can observe the effect of δ by two ways: one is disproportion of terminal chains in n.CBC.n homologues. The other is done in comparison between fluorinated isomers (pair isomers with only positional difference of substituted fluorine atom). As will be described, both ways give moderate but still meaningful effect on the phase stability.

Care must be given that the contribution of different terminal bearings structures inevitably included. Similar comparison of effect of deviation δ is observed in terphenyl-core system and no indication of vital effect of δ on the phase stability.

The comparison between fluorinated isomers (pair isomers with only positional difference of substituted fluorine atom) will be supplemental way for observing effect of δ.

Less ordered phases

In the following, we have analyzed a complex conformational isomer that will express a bent form isomer shown in Figure 3. This conformer can simulate the molecule in ordered phase at near transition to higher temperature and also just after the transition (The illustrated rotor and bearing express a state after the transition; point G is located between point O and point S).

TABLE 1 Effect of position of fluorination of the core in the paired isomers on the thermal stability of the rotor in the ordered phases.

No.	Small deviation	Large deviation
4, 5	3.clF.5[B:61.0A:99.5]	3.crF.5[C:13.0A:16.0]
7, 8	4O.crF.5[E:85.5B:86.5C:99.5]	4O.clF.5[C:96.5]
9, 10	5.clF.O6[G:78.0B:88.8C:139.5]	5.crF.O6[J:47.5C:113.5]
11, 12	4O.clF.7[B:88.8C:139.5]	4O.crF.7[E:79.2B:87.0]
13, 14	5.clF.O8[G:83.0B:100.5]	5.crF.O8[I:53.5C:116.5]
15, 16	5.llF.O6[G:176.0A:210.9]	5.rrF.O6[G:160.0C:162.0]
17, 18	5.llF.O8[G:170.5A:210.0]	5.rrF.O8[G:146.0B:158.0]
19, 20	5.lrF.O6[C:131.5]	5.rlF.O6[K:48.5J:62.0C:105.0]
21, 22	5.lrF.O8[C:137.0]	5.rlF.O8[K:25.0J:43.5C:119.0]
23, 24	5.lFF.O6[C:156.5]	5.rFF.O6[C:145.5]
25, 26	5.lFF.O8[C:155.5]	5.rFF.O8[C:144.0]

TABLE 2 Effect of the moment of inertia of ordered phases on the substituted position of fluorinated atoms in the core.

No.	Symbol	I_A(*10^{-47}) (kg m^2)	I_B(*10^{-47}) (kg m^2)	I_C(*10^{-47}) (kg m^2)	ε (Å)	δ (Å)
1	**3.5**	777	19964	20592	0.5483	1.3433
2	**5.O5**	1140	33575	34544	0.931	1.3781
3	**5.O8**	1410	43032	44256	1.0626	2.5405
4	**3.clF.5**	990	20194	20925	0.5633	1.3379
5	**3.crF.5**	1035	19983	20795	0.5959	1.3711
6	**3.crF.6**	1217	22984	23966	0.6936	1.9686
7	**4O.crF.5**	1061	26186	26589	0.6463	0.5799
8	**4O.clF.5**	1134	26014	26733	0.6721	0.7093
9	**5.clF.O6**	1393	33835	34931	0.939	1.3733
10	**5.crF.O6**	1436	33616	34782	0.9684	1.4049
11	**4O.clF.7**	1480	33818	34995	0.9599	1.7853
12	**4O.crF.7**	1554	33541	34837	0.9961	1.8217
13	**5.clF.O8**	1659	43508	44844	1.0579	2.5341
14	**5.crF.O8**	1731	43102	44544	1.0916	2.5651
15	**5.llF.O6**	1376	34869	36069	0.919	1.3796
16	**5.rrF.O6**	1430	34209	35464	0.9459	1.3823
17	**5.llF.O8**	1622	44785	46220	1.0341	2.54
18	**5.rrF.O8**	1761	43427	45000	1.0806	2.5445
19	**5.lrF.O6**	1389	34120	35318	0.9006	1.3689
20	**5.rlF.O6**	1485	33629	34929	0.9806	1.4089
21	**5.lrF.O8**	1637	43912	45345	1.0105	2.5316
22	**5.rlF.O8**	1807	42985	44596	1.105	2.558
23	**5.lFF.O6**	1605	35362	36773	0.8936	1.3729
24	**5.rFF.O6**	1750	34273	35833	0.989	1.409
25	**5.lFF.O8**	1823	45621	47239	0.9863	2.535
26	**5.rFF.O8**	2141	43383	45329	1.2221	2.5606
27	**5.CBC.5**	1307	43939	44464	0.5554	0.5024
28	**5.C.lrF.BC.5**	1568	44332	45110	0.6544	0.5996

In these cases, the center of rotor S is no more on the line that connects the two bearings. The mass of terminals in bent form will have effect on decentralization of the center of gravity G.

The calculation is conducted on the conformational molecular form illustrated in Figure 3. The calculated deviations of the center of the gravity G from the center of the core S in molecules: 3.5, 3.clF.5 and 3.crF.5 are shown in Table 1 and Table 2. Projection of the point G on to the yz-plane gives eccentricity ε and that of on to the xy-plane gives deviation δ.

We found two effects that one is that fluorination will increase eccentricity in the bent conformational form (see Figure 3) in some extent compare to the non-fluorinated ones. If we compare 3.5 and 3.clF.5 in their transition temperature of SmA phase to higher temperature phases (N or isotropic liquid phase), it is shown that around 10 to 20% reduction of transition temperature in fluorinated isomers. Calculated ε values consist of superposition of effect of fluorination and bent molecular form. This unavoidably obscures the separation of both effects on the stability of less ordered phases: SmA and SmC.

The other one is that fluorination on the core has distinct effect on deviation δ by their different positions. Substitutions of hydrogen atom in the core near to the shorter terminal chain by fluorine atom naturally give smaller deviation δ than that far from that as typically shown in Table 2. As shown in Table 1, the effect of position of fluorination in the core in the paired isomers on thermal stability of the rotor in the ordered phase is clearly contrasted: isomer with smaller deviation is always gives stable ordered phases than the isomer that has larger deviation.

Comparison of stability of SmC in each pair is straightforward if both correspondent isomers provoke SmC phases: isomer with smaller deviation δ is always gives stable SmC phases than the isomer that has larger deviation δ.

In the next section, moment of inertia that is specifically correlated parameter to the dynamics of rotation in the rotor-bearing system is analyzed in order to observe the applicability of the

mechanical model to ordered phases and higher temperature phases.

Moment of Inertia

Ordered phases

Effects of the substituted position of fluorine atom in the core are summarized in Table 2. It is assumed that the axes A, B, and C pass through the center of gravity and are perpendicular to the axes X, Y, and Z, respectively, thus I_A, I_B, and I_C represent the corresponding moment of inertia.

Comparative observation on the calculated results (Figure 3 and Table 2) for non-fluorinated compound and corresponding two fluorinated pair isomers (for example, 5.O8, 5.clF.O8 and 5.crF.O8), the fluorinated isomer with smaller eccentricity ε always associates smaller I_A value compare to that of larger ε. Similarly the fluorinated isomer with smaller δ always associates larger I_B and I_C value compare to that of larger δ.

Small eccentricity ε and small deviation δ definitely cause stability of ordered phases and also higher temperature SmC and SmA in fluorinated ones.

Nematic phase

The nematic phase can be modeled by ensemble free rotors suspended in uniaxial potential. The rotors rotate around the minimum principal axis of inertia I_A. Rotations around short axes are restricted by the uniaxial potential and enhanced such restriction by large moment of inertia I_B and I_C. Its figurative image will be fallen leaves in uniaxial gravity potential. The leaves are falling as they rotate around the minimum principal axis of inertia I_A.

Let us compare the eleven isomeric pairs that differ in only position of fluorination. As shown in Table 3, in each pair, the isomer with smaller deviation of G from S is always stable compare to that of larger one but one exception in case of pair of 4O.clF.7 and 4O.crF.7.

TABLE 3 Effects of the moment of inertia of nematic phases on the isomer pairs that differ only in the positional of fluorination.

No.	Small deviation	Large deviation
4, 5	3.clF.5[I_A:990 N:141.5]	3.crF.5[I_A:1035 N:140.6]
7, 8	4O.crF.5[I_A:1061 N:176.0]	4O.clF.5[I_A:1134 N:172.5]
9, 10	5.clF.O6[I_A:1393 N:166.5]	5.crF.O6[I_A:1436 N:162.5]
11, 12	4O.clF.7[I_A:1480 N:161.7]	4O.crF.7[I_A:1554 N:166.4]
13, 14	5.clF.O8[I_A:1659 N:161.0]	5.crF.O8[I_A:1731 N:155.0]
15, 16	5.llF.O6[I_A:1376 N:210.0]	5.rrF.O6[I_A:1430 N:201.0]
17, 18	5.llF.O8[I_A:1622 N:202.5]	5.rrF.O8[I_A:1761 N:195.0]
19, 20	5.lrF.O6[I_A:1389 N:166.5]	5.rlF.O6 [I_A:1485 N:166.0]
21, 22	5.lrF.O8[I_A:1637 N:160.0]	5.rlF.O8[I_A:1807 N:158.0]
23, 24	5.lFF.O6[I_A:1605 N:171.5]	5.rFF.O6[I_A:1750 N:166.0]
25, 26	5.lFF.O8[I_A:1823 N:166.0]	5.rFF.O8[I_A:2141 N:159.0]

Smallness of deviation of G from S or small eccentricity is advantage for free rotation of nematic rotors. A free rotor with larger eccentricity inevitably has larger radius of rotation that request larger excluded volume for the high-speed free rotation in the nematic phase. This is apparently a disadvantage for stable rotational dynamics.

The difference in nematic thermal stability between the pair isomer is small but almost a rule with only one exception in pair of 4O.clF.7 and 4O.crF.7.

Table 2 shows that in the eleven pairs, the isomers with smaller deviation of G from S possess always larger I_B and I_C compared to that of larger one. The inertia against the rotation or turn-over around molecular short axes will contribute for the stabilization of nematic phase in higher temperature.

Mass Distribution and Dynamic Impedance Matching

Mass distribution

As observed in previous section, mass concentration caused by fluorination has distinctive influence on thermal stability of ordered phases. It is natural to consider that mass distribution or mass concentration in a molecule has influence on dynamics of rotor-ensemble systems that reflects on thermal stability characteristics. Typical example is given in two hydrogen atoms substitution in a phenyl ring with fluorine atoms: 5.fFF.O6, 5.rFF.O6, 5.lFF.O8 and 5.rFF.O8. They have no ordered phases but form less ordered phases such as SmC, SmA and nematic phases. One can conclude that system with large mass concentration that bring large deviation between point S and G and large eccentricity inevitably destroys the stable and organized rotation in ordered phases.

Dynamic impedance matching between core and terminal groups

As observed in previous sub-section, mass distributions along molecular long axis are key factor for dynamics of rotor-ensemble. Here the authors insist importance of impedance matching between sub-units in the molecule. The sub-unit means any independent groups supposed to move as a unit in vibrational or rotational modes in molecular or inter-molecular motions that specifically relate to stability of rotor dynamics. For example, terphenyl derivatives: 5.rrF.O8 and 5.llF.O8, one can divide five units: alkyl(pentyl-) terminal / phenyl ring(left) / phenyl ring (center) / phenyl ring(right) / alkoxy(octyloxy) terminal. For simple quantitative analysis, we extract one parameter: mass of the sub-unit among many mechanical or dynamical parameters such as elasticity, shape, density and strain.

As an example, 5.rrF.O8 has better impedance matching between $-OC_8H_{17}$ (mass=129) and the fluorinated phenyl ring (mass=95) than that of 5.llF.O8 in which matching is 128 (alkyl terminal) to 76 (phenyl ring). The SmB phase is stable in 5.rrF.O8 but

not found in 5.llF.O8 though it gives SmC in the corresponding temperature range. As well as the impedance matching superiority of the former isomer, damping and stabilizing contribution of terminal $-OC_8H_{17}$ onto the core rotor that enable by its heavier weight than joining rotor sub-unit: fluorinated phenyl ring, is important. This results contrasted with the case in the pair isomers 5.rrF.O6 and 5.llF.O6. The isomer 5.rrF.O6 has good impedance matching between $-OC_6H_{13}$ (mass=101) and the fluorinated phenyl ring (mass=95). Damping and stabilizing contribution of terminal $-OC_6H_{13}$ onto the core rotor can not be expected.

Molecular Conformations and Dynamic Behaviors of Molecular Ensemble

Fluorination on specific positions in terphenyl core has introduced mechanical and dynamical effects on phase behaviours as already described in previous sections. Addition to these distinct effects, complement consideration on another fluorination effect, i.e. potentiality of conformational changes induced by fluorination on specific positions in terphenyl core should be discussed. Size of fluorine atom is 10% larger than hydrogen atom. Even so, fluorine substitution will cause increase in angle between the planes of neighbor phenyl-rings by ortho-fluorine substitution.

TABLE 4 Mechanical and dynamical effects on phase behaviors dependent on fluorination positions in terphenyl ring.

	meta (F/-OR)	*ortho* (F/-OR)
R=C_6H_{13} (5.rlF.O6/5.rrF.O6)	K:48.5J:62.0C:105.0N:166.0	G:160C:162
R=C_8H_{17} (5.rlF.O8/5.rrF.O8)	K:25.0J:43.5C:119.0N:158.0	G:146.0B:158.0A:195.0

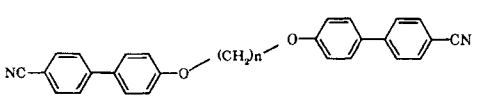
Let us considers the two isomeric pairs shown in Table 4. Fluorination of 2-position of terminal phenyl ring (5.rlF.O6; 5.rlF.O8) gives rich polymorphism compare to that of 3-position (5.rrF.O6;

5.πF.O8) as seen in Table 4. The former isomer has higher potentiality for various conformational isomerism. It must be also mentioned that 4-positon is substituted by alkoxy terminal chains (hexyloxy- or octyloxy-). Compared to the alkyl terminal chains, the alkoxy-terminal chains have larger potentiality for elongation apart from the plane of adjacent fluorinated phenyl ring. This potentiality will allow possibility for conformational complexity of the former isomers.

Freedom of conformation accompanies rich polymorphism. This is an experienced rule, but a general mechanical model for liquid crystal ensemble that proposed by the authors at the Japanese Liquid Crystal Conference in 1999 [14] given a basic reasoning for it (a paper will be published elsewhere).

Thermal Behaviors of Liquid Crystalline Oligomers

In this section we examine interesting liquid crystalline oligomers such



α, ω-bis(4,4'-cyanobiphenyloxy) methylenes

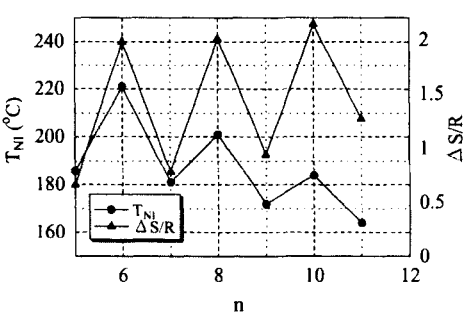


FIGURE 4 Structure of the oligomers and the properties of T_{NI} and $\Delta S/R$. Where $\Delta S/R$ is the entropy; n the amount of carbon in core.

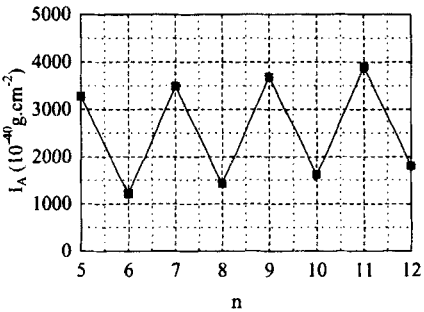


FIGURE 5 Relation between the moment of inertia I_A and n.
Where n is amount of carbon in

as α, ω-bis (4,4'-cyanobiphenyloxy) methylenes. The transitional temperature of isotropic-nematic phase T_{NI} and transitional entropy $\Delta S/R$ are shown as Figure 4 in which there is a well known odd-even effect. Explaining this thermal phenomenon, we used the semiempirical molecular orbital package for the study of the moment of inertia of the molecules (see Figure 5) in which it has also clearly odd-even effect. The comparison of Figure 4 and Figure 5 is made and we can see that the ability of rotor is mutually related with the transitional entropy at isotropic-nematic phase, namely, the transitional entropy increases when the moment of inertia increases. A good rotor-bearing system will remain its order just before the transitional temperature.

CONCLUSION

It is applied a molecular mechanical model: rotor-bearing and free rotor models onto terphenyl- and fluorinated terphenyl liquid crystals. The phenomena of thermal stability of phase and phase transition are interpreted by fundamental mechanical and dynamical parameters: center of gravity, eccentricity, mass distribution and moment of inertia.

Fluorination effects on liquid crystallinity are explained in uniform manner by mechanical and dynamical basis. Moreover, the characteristic thermal behaviors of the liquid crystal oligomers are examined, and are correlated to the molecular structures and their mechanical or dynamical parameters to complete validity of the model proposed.

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