Interpretation of the odd-even behavior for the emergence of ferroelectricity and antiferroelectricity in bent-core mesogens

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Simple theoretical interpretation has been made on the previously reported odd-even behavior of the emergence of ferroelectricity and antiferroelectricity in homologous series of bent-core mesogens with the same chiral end chains (S,S); compounds with even and odd carbon numbers (including oxygen) exhibit ferroelectric and antiferroelectric $B2$ phases, respectively. The odd-even behavior was confirmed in newly synthesized racemic compounds with chiral end chains of R and S forms (R,S) together with (R,R) and (S,S) forms. According to our theoretical interpretation, ferroelectricity should be more stable in (R,S) compounds than in (S,S) compounds. Actually, the transition temperature from the isotropic phase to the Sm-CP phase was higher and the temperature range of the $B2$ phase was broader in the (R,S) compound than in the (S,S) compound.

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I. INTRODUCTION

Since Niori *et al.* [1] discovered that achiral bent-core (banana shaped) molecules possess unusual and interesting properties, i.e., unique polarity and supramolecular chirality, much attention has been paid to these materials [2]. From the viewpoint of fundamental materials researches, it is very important to understand the relationship between molecular structures and mesomorphic properties. In this respect, the syntheses of a series of liquid crystals with systematic structural variation are crucial to examine this relationship between the chemical structures and their physical properties. Among eight phases, $B1-B8$ [2], the most widely studied is the $B2$ phase, in which four structures are known to exist depending on tilt and polar correlations between adjacent layers [3]; Sm-$C_{S,A}P_{F,A}$. Here the first two subscripts, S and A, specify syn- and anticlinicity, and the second two subscripts, F and A, specify ferro- and antiferroelectricity, respectively. Not so many ferroelectric bent-core mesogens have been reported [4–15]. In addition, some metastable ferroelectric phases, which are induced by applying an electric field to the antiferroelectric state, have also been reported [16–19]. However, as in Pn-O-PIMB with achiral terminal alkoxy chains, most of bent-core mesogens exhibit the antiferroelectric mesophase [20–24]. This is quite natural from the viewpoint of interlayer steric interaction. Namely, Sm-C_SP_A is the only structure satisfying the condition that the terminal chains in adjacent layers are parallel to each other. An intentional attempt to suppress Sm-C_SP_A and to obtain the ferroelectric phase was made by Walba *et al.* [25] by introducing the same chiral terminal chain as that of a material (MHPOBC) showing the smectic-C_A* (Sm-C_A*), anticlinic organization of rodlike molecules.

Recently we reported that the emergence of ferroelectricity and antiferroelectricity depends upon the number of carbons and the position of the chiral carbon along the terminal chains in the banana-shaped molecules [Pn-O-PIMB$(n-2)$*,

Fig. 1(a)], where n stands for the number of carbons in each end chain and $(n-2)$* for the chiral position from the oxygen next to the core; namely, the third carbon from the chain end (methyl carbon) is always chiral [26–29]. The compound exhibits ferroelectric Sm-C_AP_F* phase when n is even, whereas it exhibits antiferroelectric Sm-C_SP_A* phase when n is odd. Besides, the odd-even behavior was also observed in the Pn-O-PIMB$(n-2)$*$-(n-4)$O [Fig. 1(b)] [30,31]. Here, the oxygen, which is located at the $(n-4)$th position from the oxygen next to the core, is regarded as a carbon when count-
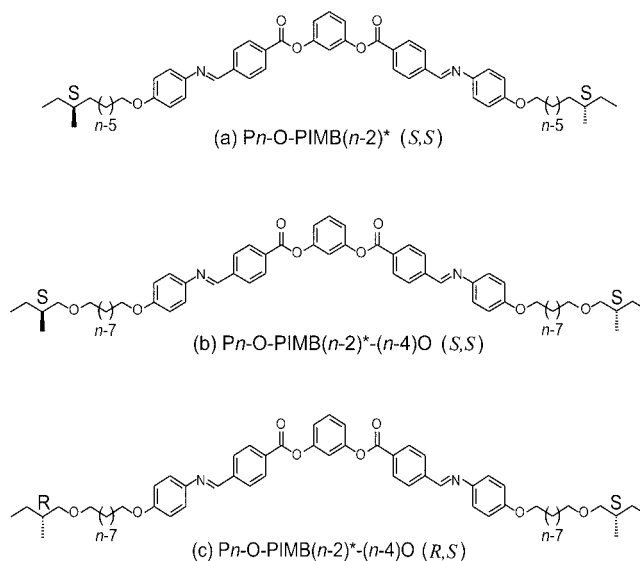

FIG. 1. The chemical structures of (a) (S,S)Pn-O-PIMB$(n-2)$*, (b) (S,S)Pn-O-PIMB$(n-2)$*$-(n-4)$O and (c) (R,S)Pn-O-PIMB$(n-2)$*$-(n-4)$O. (a) and (b) are previously reported compounds [28,30], which exhibit the odd-even behavior, i.e., ferroelectric phase for n=even and antiferroelectric phase for n=odd, and (c) is the compounds synthesized and investigated in this paper.

ing the number of the carbons in the each end chain. The odd-even effect observed in the two homologous series implies that simple consideration based on the interlayer steric interaction is not sufficient to interpret the phase behavior. In this paper, we develop a theoretical formula including not only the interlayer steric interaction but also a dipole-dipole interaction and induced dipole-dipole interaction (van der Waals) to elucidate the polar order and tilt order between adjacent layers. To convince the developed theory experimentally, we synthesized the compounds (R,S)Pn-O-PIMB$(n-2)^*$-$(n-4)$O, $n=9$ (P9 in short) and 10 (P10 in short), which have the opposite configuration chiral carbons in each end chain (meso compounds), shown in Fig. 1(c), and investigated the phase structures. The absolute configuration of the chiral carbon was always "S" type in both of the previous homologues. Judged by the newly developed theory, (R,S)P10-O-PIMB8$^*-$6O must have more stable ferroelectricity than the (S,S) analog. Here we report that this is actually proved experimentally.

II. RESULTS AND DISCUSSION

The description of the experimental procedure along with spectral data for the chiral (S,S)-Pn-O-PIMB$(n-2)^*$-$(n-4)$O prepared from (S)-(-)-2-methyl-1-butanol can be found in supporting information of Ref. [30]. Racemic Pn-O-PIMB$(n-2)^*$-$(n-4)$O was prepared from racemic 2-methyl-1-butanol using the similar procedure. Thus, the present compounds include a meso compound (R,S) in addition to racemic compounds (S,S), and (R,R). Hereafter (R,S) compound means such a mixture compound.

The transition temperatures of (R,S)P9-O-PIMB7$^*-$5O and (R,S)P10-O-PIMB8$^*-$6O determined by differential scanning calorimetry (DSC) are I(140.0 °C) B2 (109.3 °C) Cry on cooling and Cry (123.3 °C) B2 (148.0 °C)I on heating for P9 and I(132.4 °C) 2 (110.8 °C) Cry on cooling Cry (124.3 °C) B2 (139.5 °C)I on heating for P10. The switching behavior of these compounds was observed using a polarizing microscope. Tristable and bistable switchings were observed for P9 [Fig. 2(a)] and P10 [Fig. 2(b)], respectively. For P9, fine stripes along the smectic layer were observed in the absence of a field, suggesting that the ground state is Sm-$C_S P_A$ and the field-induced state is Sm-$C_A P_F$ [32,33]. For P10, extinction directions are always parallel or perpendicular to the polarizer and analyzer directions, although the birefringence color changes slightly between the field-induced state and the zero-field state, as shown in Fig. 2(b). Hence, the bistable states are Sm-$C_A P_F$, in which the splayed polarization (twisted director) orientation is realized in the absence of a field [34].

The compound P9 was second-harmonic generation (SHG) inactive, but SHG was induced by the application of a field. The applied field dependence of the SHG intensity was measured using an Nd:YAG laser (10 Hz, 6 ns, 1064 nm, 10 mJ/pulse). The applied field direction was along the cell normal and the incidence angle of the laser beam was 45°. The observed hysteresis curve shown in Fig. 3 indicates the field-induced antiferroelectric-ferroelectric transition. As
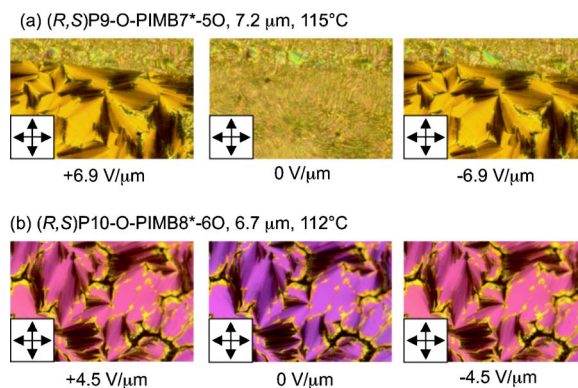

(a) (R,S)P9-O-PIMB7*-5O, 7.2 μm, 115°C

+6.9 V/μm   0 V/μm   -6.9 V/μm

(b) (R,S)P10-O-PIMB8*-6O, 6.7 μm, 112°C

+4.5 V/μm   0 V/μm   -4.5 V/μm

FIG. 2. (Color online) The switching behavior of (R,S)P9-O-PIMB7*-5O and (R,S)P10-O-PIMB8*-6O observed by polarizing microscopy. The tristable switching was observed for P9 and the bistable switching for P10, suggesting the antiferroelectric and ferroelectric phases, respectively.

suggested by the texture and switching measurements, the ground state of P9 is the antiferroelectric Sm-$C_S P_A$ state. In contrast, the compound P10 is SHG active even in the absence of an electric field. The temperature dependence of the SHG intensity is shown in Fig. 4, showing the SHG activity in the B2 phase temperature range in P10. The switching current measurements were made in P10 and a single polarization reversal current peak was observed, as shown in Fig. 5. All these results are consistent with the conclusion made by the texture and the electrooptic measurements; i.e., P10 is the ferroelectric Sm-$C_A P_F$ state. Thus, the odd-even behavior was also observed in the (R,S) compounds. One of the remarkable difference between (S,S) compound and (R,S) compound is the clearing point and the temperature range of the B2 phase; i.e., they are respectively 124.3 °C and 17.1 °C for (S,S) and 128.3 °C and 23.5 °C for (R,S) Sm-$C_A P_F$ and 137.1 °C and 27.0 °C for (S,S) and 140.2 °C, and 30.5 °C for (R,S) Sm-$C_S P_A$.
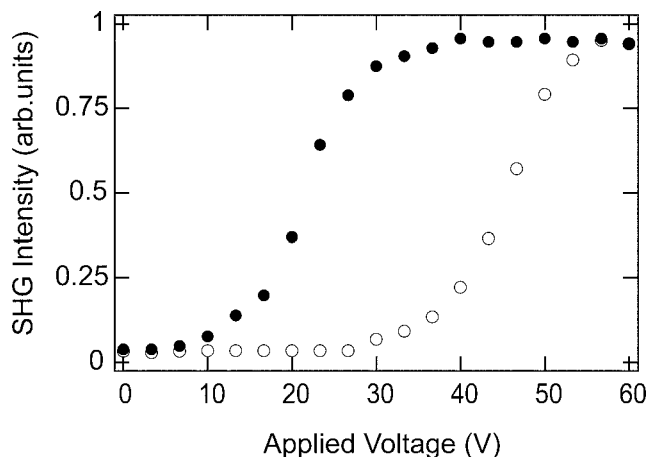
FIG. 3. The SHG intensity as a function of applied field in a 9.2 μm-thick cell of (R,S)P9-O-PIMB7*-5O at 120 °C. A hysteresis curve was observed, indicating the field-induced antiferroelectric to ferroelectric transition. Open and closed symbols stand for the data taken with increasing and decreasing voltage respectively.
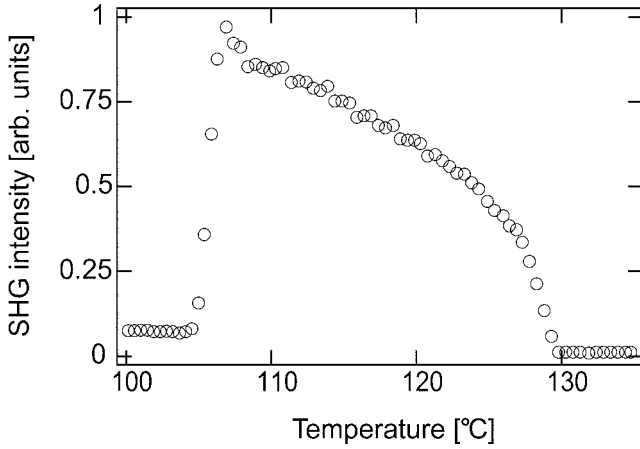
FIG. 4. The SHG intensity as a function of temperature in an 8.0 μm-thick cell of (R,S)P10-O-PIMB8*-6O in the absence of an electric field. The SHG activity without an electric field indicates the polar order.

III. THE MECHANISM OF THE ODD-EVEN BEHAVIOR

In our previous paper [30], we attributed the odd-even behavior to the direction of the methyl group, which is connected to the chiral carbon, and suggested the importance of the interlayer interactions of the end chains for this behavior. Here we developed the theoretical consideration by including the "steric interaction," "dipole-dipole interaction" and "van der Waals attraction."

A. Theoretical formula

Free energy of a smectically ordered noncolumnar banana phase is expressed with polarization $\mathbf{P}_j$ and tilt order parameter ξ_j for the jth smectic layer [35], as

$$G = \sum_{j=1,2} \left(\frac{1}{2}a_{0p}\mathbf{P}_j^2 - \frac{1}{4}|b_{0p}|\mathbf{P}_j^4 + \frac{1}{6}c_{op}\mathbf{P}_j^6 + \frac{1}{2}a_{0t}\xi_j^2 + \frac{1}{4}b_{0t}\xi_j^4 \right.$$
$$\left. - \frac{1}{2}|\Omega|(\xi_j \times \mathbf{P}_j)^2 \right) + \frac{1}{2}a_{1p}(\mathbf{P}_1 \cdot \mathbf{P}_2) + \frac{1}{2}a_{1t}(\xi_1 \cdot \xi_2). \quad (1)$$

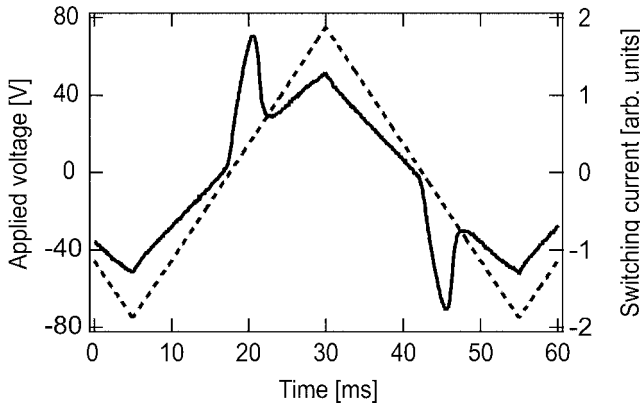Subscripts p and t remind the reader that interactions are

FIG. 5. The polarization reversal current under the application of a triangular-wave voltage (130 V$_{PP}$, 20 Hz) in a 6.7 μm-thick cell of (R,S)P10-O-PIMB8*-6O at 112 °C. A single switching current peak was observed, indicating the ferroelectric phase.

expressed in polarization and tilt, respectively. Number 0 in a subscript denotes intralayer interactions and 1 denotes interactions between nearest neighboring layers. In Eq. (1) the only temperature dependent coefficient is $a_{0p}=\alpha(T-T_0)$ and the rest of coefficients are taken as constants typical for a material. Generally the I-Sm transition is of the first order. Therefore we consider b_{0p} as negative and c_{0p} as positive. Similarly, the tilt can also become critical. However, in banana systems the driving mechanism for forming the phase structures is the polar order and both a_{0t} and b_{0t} are considered as positive and constant. The coefficient Ω is negative, since tilt in the direction perpendicularly to the polarization is most favorable. The two coefficients a_{1p} and a_{1t} can have either negative or positive signs. Negative signs favor ferroelectric or synclinic order, respectively, and positive signs favor antiferroelectric or anticlinic order. The classical banana compounds Pn-O-PIMB which does not have the chiral carbon exhibit the antiferroelectric Sm-C_SP_A phase and the compounds Pn-O-PIMB$(n-2)^*$(n=even) exhibit the ferroelectric Sm-C_AP_F phase by introducing the chiral carbon in the third position from the chain end. As clinicity as well as polarity differs in such compounds with and without the chiral groups, it is clear that these chiral groups on the molecular tails mainly affect the interlayer interactions given by a_{1p} and a_{1t}.

B. Polarity

The polar order in neighboring layers (ferroelectric and antiferroelectric) is a consequence of the competition between three types of interactions: steric interaction, dipole-dipole interaction and van der Waals attraction. The steric interaction favors that end chains are parallel in the layer boundary, which allows partial interlayer diffusion (interdigitation) of end chains. In this case, the polar order is antiferroelectric [Fig. 6(a)] and the steric interaction stabilizes the antiferroelectric phase. The dipole-dipole interaction favors that the dipole moments in neighboring layers are antiparallel [36]. Therefore, also the dipole-dipole interaction stabilizes the antiferroelectric phase. These two interactions give positive contribution to the coefficient a_{1p}.

In order to analyze the effects of the van der Waals attraction, we consider that the molecule consists of interacting parts and which all contribute to the effective van der Waals attraction between the elements. In this case, the distances between the contributing parts are shorter in the ferroelectric than in the antiferroelectric phase [Fig. 6(b)]. Therefore the van der Waals attraction stabilizes the ferroelectric phase and contributes negatively to coefficient a_{1p}. When the contribution of the van der Waals attraction is more important than the contributions of the steric interaction and the dipole-dipole interaction, the a_{1p} is negative and the ferroelectric phase is stable. If the opposite is true and the steric interaction and the dipole-dipole interaction are more important than the van der Waals attraction, the a_{1p} is positive and the antiferroelectric phase is stable.

C. Clinicity

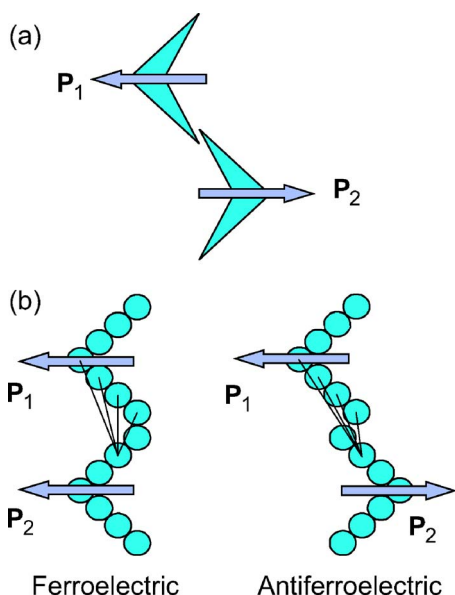For the clinicity, the two contributions are important namely the steric interaction and the van der Waals attrac-

FIG. 6. (Color online) Schematic illustration of three contributions to the polar order. (a) The steric interaction favors antiferroelectric order, as partial interdigitation of end chains is allowed. The dipole-dipole interaction also stabilizes the antiferroelectric order, as favorable orientation of dipoles in neighboring layers is antiparallel. (b) The van der Waals attraction between interacting molecular bonds (parts presented by circles) stabilizes the ferroelectric order as the distances between interacting parts are shorter than those in the antiferroelectric order.

tion. The steric interactions favor the parallelism of end chains in the planes not only parallel but also perpendicular to the polarization [Fig. 7(a)]. The tilting correlations in the plane parallel to the polarization are shown in dotted boxes. Here, tilt senses toward and away from readers are specified by thick and thin molecular ends, respectively. The Sm-$C_S P_A$ structure allows interdigitation of end chains and the contribution to the coefficient a_{1t} is negative, since the parallelism is held in both planes. On the other hand, in the Sm-$C_A P_F$ structure, the end chains are not parallel in both planes. Hence, this is the most unstable structure from the steric interaction viewpoint and the contribution to the coefficient a_{1t} is positive. As for the Sm-$C_S P_F$ and Sm-$C_A P_A$ structures, the end chains are not parallel in either of the planes. For simplicity the Sm-$C_S P_F$ and Sm-$C_A P_A$ structures are categorized into negative and positive a_{1t}. This is not essentially important, however, since either of the Sm-$C_S P_A$ or Sm-$C_A P_F$ structure emerges and neither the Sm-$C_S P_F$ nor Sm-$C_A P_A$ structures emerge in the studied homologous series of the bent-core molecules.

The van der Waals attraction has the opposite effect. The distances between the interacting molecular parts are shorter in the anticlinic structure than in the synclinic phase [Fig. 7(b)]. As a result, for the condition prevailing the van der Waals attraction the coefficient a_{1t} is positive and the anticlinic phase is stable. For the condition prevailing the steric interaction, on the contrary, the coefficient a_{1t} is negative and consequently, the synclinic phase is stable. The stable phase structure changes according to their signs of the parameters a_{1p} and a_{1t} (Table I).
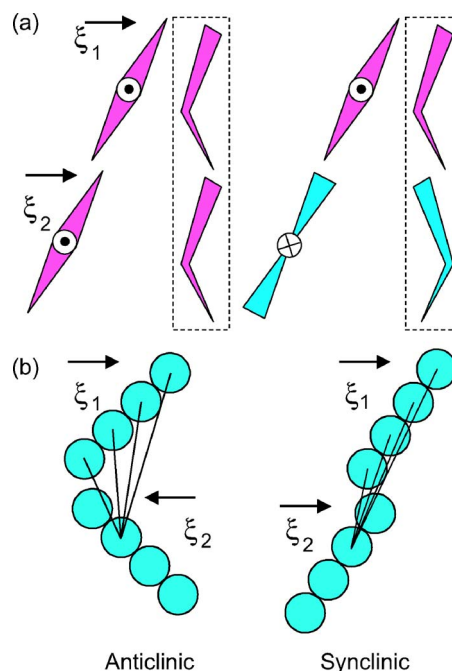

FIG. 7. (Color online) Schematic illustration of two contributions to the clinicity. (a) steric interaction stabilizes the synclinic phase and (b) van der Waals attraction stabilizes the anticlinic phase. The views in (a) are for both planes perpendicular and parallel (in dotted boxes) to the polarization direction. In the views in dotted boxes, another conflict for the interlayer diffusion (interdigitation) is noticed even in the synclinic structure (left).

D. The direction of the methyl group and theoretical interpretation

In the previous simple model shown in Figs. 6 and 7, the effect of the direction of the methyl group connected to the chiral carbon was not taken into account in the van der Waals attraction and the steric interaction. However, it is obvious that the direction affects the van der Waals attraction as well as the steric interactions. According to our previous calculation [30], in which most stable molecular conformations were determined by the Spartan'02 program [36] using two neighboring molecules, the direction of the methyl group of the Pn-O-PIMB$(n-2)^*$ with even n is outside of the layer, and that with odd n within the layer. We repeated the calculation using a single wing of the molecules, i.e., between the phenyl core and the end chains. Because of many bonds, about which rotation is possible, a variety of conformations are possible and moreover the energy minima of these conformations are more or less the same. However, we con-

TABLE I. The stable phase structures determined by the parameter a_{1p} and a_{1t}. The structures in parentheses are stable under the assumption of considering the tilting order in the plane perpendicular to the polarization.

	$a_{1t}<0$	$a_{1t}>0$
$a_{1p}<0$	(Sm-$C_S P_F$)	Sm-$C_A P_F$
$a_{1p}>0$	Sm-$C_s P_A$	(Sm-$C_A P_A$)

firmed that the number of stable conformations with the methyl group pointing outward is larger in Pn-O-PIMB($n-2$)* with even n than in Pn-O-PIMB($n-2$)* with odd n. Since the van der Waals attraction is only the possible interaction to stabilize the ferroelectric structure among the three interactions considered, as mentioned above, and the methyl group may critically influence the van der Waals attraction, we will proceed the discussion based on the conformational difference in the direction of the methyl group for the compounds with even n and odd n.

How does the direction of the chiral carbon influence the polarity and clinicity? The experimental result reveals that Pn-O-PIMB($n-2$)* with even n exhibits the ferroelectric order, and that with odd n exhibits the antiferroelectric order. It is obvious that the dipole-dipole interaction is not significantly influenced by the direction of the methyl group. In the previous simple model shown in Figs. 6 and 7, the effect of the direction of the methyl group was not taken into account in the van der Waals attraction and the steric interaction. However, this direction affects the van der Waals attraction as well as the steric interactions.

Let us first consider these interactions in Pn-O-PIMB($n-2$)* with even n and that with odd n. The interdigitation of end chains is obstructed, if the chiral carbon points outside of the layer [Fig. 8(a)]. Hence, the negative contribution to the coefficient a_{1p} is smaller in Pn-O-PIMB($n-2$)* with even n. On the other hand, the interdigitation is not seriously obstructed by introducing the methyl group, if the group is within the layer [Fig. 8(b)] in Pn-O-PIMB($n-2$)* with odd n. Therefore, from the viewpoint of the steric interaction, ferroelectric structure is destabilized in Pn-O-PIMB($n-2$)* with even n, contradicting to the experimental fact [28,30]. To overcome this contradiction, one can consider the effect of the van der Waals attraction. The distance between the methyl groups of the molecules in the neighboring layers is closer in Pn-O-PIMB($n-2$)* with even n than that in Pn-O-PIMB($n-2$)* with odd n, since the direction of the methyl group in the former compounds is outside of the layer [Fig. 8(a)] whereas that in the latter compounds is inside of the layer [Fig 8(b)]. Therefore, the negative contribution to the coefficient a_{1p} is larger in Pn-O-PIMB($n-2$)* with even n than in Pn-O-PIMB($n-2$)* with odd n. Thus, the van der Waals attraction stabilizes the ferroelectric structure more in Pn-O-PIMB($n-2$)* with even n than in Pn-O-PIMB($n-2$)* with odd n. Therefore, if the contribution of the methyl group to the van der Waals attraction is stronger than to the steric interaction, the odd-even effect experimentally observed is explained in the context of the present theoretical consideration.

Similar consideration is valid for clinicity, as shown in Fig. 9. The experimental result shows that Pn-O-PIMB($n-2$)* with even n exhibits the anticlinic phase, and that of (n=odd) exhibits the synclinic phase, as highlighted by dotted boxes. Again, for Pn-O-PIMB($n-2$)* with even n the steric interactions are less important than the van der Waals attraction due to the obstruction of the interdigitation, which results in the positive coefficient a_{1t}. The anticlinic structure is therefore stable. However, the promoted interdigitation for Pn-O-PIMB($n-2$)* with odd n results and consequently the
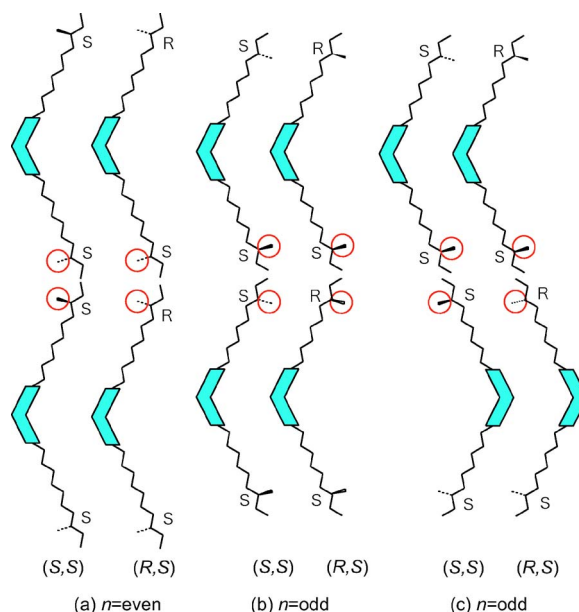

FIG. 8. (Color online) The schematic illustration of the ferroelectric order in compounds with (a) even n and with (b) odd n to consider the magnitudes of the steric interaction and the van der Waals attraction. The interdigitation is more obstructed in the compounds with (a) even n than that with (b) odd n, suggesting that the ferroelectricity is more stable in the compounds with (b) odd n, contradicting to the experimental fact. However, van der Waals attraction stabilizes the ferroelectricity more in the compounds with (a) even n, as follows: In (a), the distance between the methyl groups of the neighboring molecules in adjacent layers becomes closer than that in (b). The magnitude of the van der Waals attraction in the compounds with (a) even n becomes larger than that with (b) odd n because of the closer distance of neighboring methyl groups. Similar argument leads to the conclusion that the compounds with odd n stabilize the antiferroelectric structure (c). If we compare the "van der Waals attraction" in the (S,S) and (R,S) compounds with (a) even n, two methyl groups in adjacent layers are closer in (R,S) compounds, since both methyl groups direct backward of the paper plane. Therefore, the ferroelectric structure is more stable in the (R,S) compounds.

prevailing steric contribution (negative a_{1t}) stabilizes the synclinic ordering. The van der Waals attraction also favors the synclinic ordering for Pn-O-PIMB($n-2$)* with odd n.

Shortly, if the methyl group has such a direction that prevents the interdigitation of molecular end chains, the Sm-$C_A P_F$ structure is favorable. If the interdigitation of end chains is not obstructed due to the direction of the methyl group, the Sm-$C_S P_A$ phase is stabilized. The theoretical consideration is therefore consistent with the experimental results ever obtained [28,30]. In the (R,S) compounds, the partial interdigitation of the end chains is even more obstructed due to the direction of the methyl groups as chiral carbons of R and S type molecules are close to each other in the layer boundary [Fig. 8(a)]. Therefore the ferroelectric phase is even more stable. The closer methyl groups also promote the van der Waals attraction. Thus, this effect also stabilizes the ferroelectric phase. Actually, the clearing temperature is higher in the (R,S) P10-O-PIMB8*-6O compound than the (S,S) compound, and the temperature range
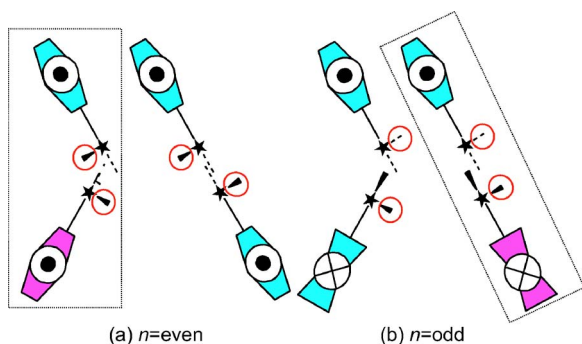
FIG. 9. (Color online) The schematic illustration of the magnitude of the van der Waals attraction for the clinicity. In the compounds with (a) even n, the van der Waals attraction becomes larger in the Sm-$C_A P_F$ structure (in dotted box) than in the Sm-$C_S P_F$ structure. On the other hand, in the compounds with (b) odd n, the Sm-$C_S P_A$ structure becomes more stable due both to the steric interaction and the van der Waals attraction.

of the Sm-$C_A P_F$ phase of the (R,S)P10-O-PIMB8*-6O is wider than that of the (S,S)P10-O-PIMB8*-6O. The Sm-$C_A P_F$ phase is stable between 132.4 °C to 110.8 °C (interval 21.6 °C) in (R,S)P10-O-PIMB8*-6O, while it extends from 128.3 °C to 110.8 °C (interval 17.5 °C) in (S,S)P10-O-PIMB8*-6O, both on cooling.

Then how about the Sm-$C_S P_A$ phase? As same as the Sm-$C_A P_F$ phase, mentioned above, the Sm-$C_S P_A$ phase is also stabilized in the (R,S)P9-O-PIMB7*-5O compound than that in the (S,S) compound. Namely, the clearing temperature is higher in the (R,S)P9-O-PIMB7*-5O compound than the (S,S) compound, and the temperature range of the Sm-$C_S P_A$ phase of the (R,S)P9-O-PIMB7*-5O is wider than that of the (S,S)P9-O-PIMB7*-5O. The Sm-$C_S P_A$ phase is stable between 140.0 °C to 109.3 °C (interval 30.7 °C) in (R,S)P9-O-PIMB7*-5O, while it extends from 138.3 °C to 111.2 °C (interval 27.1 °C) in (S,S)P9-O-PIMB7*-5O, both on cooling. From the viewpoint of the steric interaction, the Sm-$C_S P_A$ phase is more stable in (R,S)P9-O-PIMB7*-5O because of the relationship of two methyl groups. However, it is more stable in (S,S)P9-O-PIMB7*-5O from the van der Waals interaction, because of the closer methyl groups. The experimental result suggests that the effect of the steric interaction is dominant. However, because of these competing interaction, the rate of phase stabilization by introducing (R,S) is a little smaller in P9-O-PIMB7*-5O than in P10-O-PIMB8*-6O.

Further studies including systematic syntheses of related compounds are required. Actually we already reported that the *B*2 phases in the homologues (Pn-O-PIMB5*-4O, n=7, 8, 9, and 10) with chiral 3-(alkoxy)propoxy terminal groups $CH_3(CH_2)_m C^* H(CH_3)O(CH_2)_3 O$- ($n=m+6$) show, without exception, the antiferroelectric Sm-$C_S P_A$* state [37]. In these homologues the position of the chiral center (the methyl group) is fixed at the position number 5 (odd) from the phenoxy oxygen in the terminal group. Homologues with the methyl group positioned at 6 (even), Pn-O-PIMB6*-5O with $CH_3(CH_2)_m C^* H(CH_3)O(CH_2)_4 O$- ($n=m+7$), are expected to show the ferroelectric Sm-$C_A P_F$* state. The synthesis of this series of mesogens is currently in progress.

The consideration presented here for the cause of stabilization of the ferroelectric state might be applicable to other systems. For example, it seems that in the compounds of Ref. [6] the bulky groups attached to the terminal chain would obstruct the interdigitation and, as a consequence, the van der Waals interaction would be dominant. Further examination is beneficial for designing compounds showing the ferroelectric state in banana mesogens.

IV. CONCLUSIONS

We have investigated the phase structure of the compounds of Pn-O-PIMB$(n-2)$*-$(n-4)$O (n=9 and 10) with (R,S) chiral carbons in the end chains and have shown that the odd-even behavior is also present in the (R,S) compounds. Namely odd n (n=9) and even n (n=10) compound exhibit antiferroelectric and ferroelectric phases, respectively. We clarified the mechanism of the odd-even behavior by taking into account the direction of the methyl groups which are connected to the chiral carbon. Considering the influences of the steric, dipole-dipole, and van der Waals interactions on the polar and tilt order, it is clarified that in the (R,S) compounds the ferroelectric Sm-$C_A P_F$ phase is more stable than in chiral compounds. Actually the observed temperature range of the *B*2 phase in meso compounds is wider than that of the compounds that have the same chiral carbon configuration and the clearing temperature in the (R,S) compounds are higher than the (S,S) compounds.

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