Effect of flexible bimesogen dopant on the stability of the anticlinic liquid-crystal phase

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Small quantities of the floppy bimesogen di(4PPB5)3Si were dissolved in an anticlinic liquid crystal consisting of a mixture of left-handed and right-handed TFMHPOBC, with enantiomer excess $X=0.2$. The bimesogen dopant was found to promote anticlinic order with an anticlinic interaction coefficient per molecule u_{dopant} smaller than, but of the same order as, that of the rigid bent-core dopant P-7PIMB. For both dopants u_{dopant} was found to be much larger than that due to a pair of TFMHPOBC molecules in adjacent layers. The results are examined in terms of both the flexibility of the group linking the two legs of each dopant, as well as their chemical structure.

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In recent years there has been much interest in the effects of rigid bent-core dopant molecules—these are sometimes referred to as "banana" or "bow-shaped"—dissolved in calamitic liquid crystal matrices [1–7]. Gorecka *et al.*, for example, examined the behavior of a mixture of bent-core molecules dissolved in a liquid crystal that has a synclinic Smectic-C^* (Sm-C^*) phase [5]. Here the asterisk denotes that the molecule is chiral. The bent-core mesogens were found to promote anticlinic Smectic-C_A^* (Sm-C_A^*) order over synclinic order, as the bent-core symmetry axis lies parallel to the interface between adjacent smectic layers and the bent-core plane lies parallel to the tilt plane of the anticlinic phase. More recently we examined a reentrant anticlinic to synclinic transition of an entantiomeric mixture of TFMHPOBC (Fig. 1) on a temperature-electric field phase diagram in the presence of the rigid bent-core dopant P-7PIMB (Fig. 2). As part of that work we obtained the interaction coefficient U as a function of temperature T, electric field E, and dopant concentration C [7]. Here U is the polar tilt angle θ-dependent coefficient of the free energy term $F_U = U/2[\cos(\varphi_{i-1}-\varphi_i)+\cos(\varphi_i-\varphi_{i+1})]$ that promotes anticlinic order relative to synclinic order [8], where φ_i is the azimuthal angle of the average molecular orientation in smectic layer i. We found that the interaction potential associated with the addition of one bent-core P-7PIMB molecule to the mixture is $u_{P\text{-}7PIMB} \sim 10^{-15}$ erg, which is much larger—by a factor of approximately 50—than that of a pair of calamitic TFMHPOBC molecules in adjacent layers at the Sm–C^*–Sm-C_A^* phase transition.

Despite the relatively large magnitude of $u_{P\text{-}7PIMB}$, it is still much smaller than the thermal energy k_BT, where k_B is Boltzmann's constant. However, with an appropriately designed dopant it would seem possible that the interaction energy per dopant molecule u_{dopant} might approach k_BT. Let us consider a *gedanken* experiment. We hypothesize that the important in-plane interactions between the tilts of the molecules (both liquid crystal and dopant) are mediated primarily by the interactions between their rigid-rod segments. We consider next a highly idealized dopant consisting of a spacer with two rigid rods attached at either end. Furthermore, we suppose that the dopant's spacer has a length equal to that of the alkyl region at the interface between two smectic layers, and that the spacer mixes well with the liquid crystal molecules' alkyl groups. Moreover, the spacer rigidly maintains the legs of the dopant at an angle $\Theta=90°$. Finally, these rod segments are at an angle of 45° to the spacer. While this is a highly idealized picture of a dopant it probably is approximated reasonably well by a core consisting of an alkyl chain containing an odd number of carbons and of the correct length that is attached appropriately to two rigid rod segments serving as legs. This idealized dopant, by assumption, will segregate with its rigid-rod segments, i.e., the legs, in proximity to the rigid segments of the host liquid crystal molecules. We presume that it is the interactions between the rigid-rod segments that are responsible for the in-plane elastic interactions. For this idealized dopant, which has the rigid-rod part at a polar angle of 45° to the layer normal, the interaction with the mesogens in each layer is expected to be

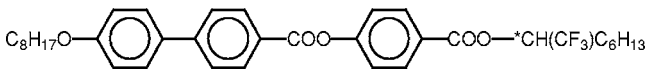

FIG. 1. Structure of TFMHPOBC.

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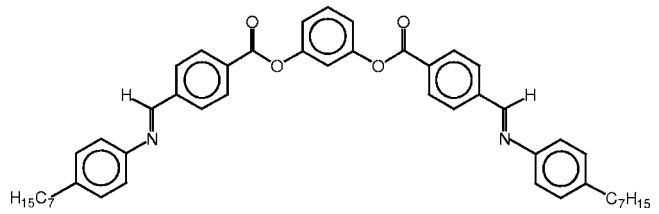

FIG. 2. Structure of bent-core molecule P-7PIMB.

$k_BT \sin\theta\cos(\varphi-\phi_d)$, where ϕ_d is the azimuthal angle of the rigid rod segment of the dopant. Calculating the resulting free energy, integrating over the possible angles of the dopant, we find $u_{dopant} \sim k_BT \sin^2\theta$.

This thought experiment suggests that u_{dopant} depends on the precise structure of the dopant, and that real bent-core dopants will possess some (but not all) all of the traits associated with our idealized dopant. From our previous work we note that P-7PIMB has a rigid core structure with $\Theta \sim 127°$ [9] associated with the spacer group, as well as legs consisting of a rigid segment terminating in a long alkyl tail. In consequence the rigid dopant core tends to segregate with the flexible end group of the TFMHPOBC molecules [6]. Moreover, the rigid part of the dopant's legs is shorter than the rigid part of the TFMHPOBC molecule, and therefore part of the dopant's flexible alkyl termination group will reside in proximity to the rigid part of the TFMHPOBC. Nevertheless, the dopant should still promote an anticlinic tendency in adjacent smectic layers, but the interaction coefficient $u_{P\text{-}7PIMB}$ should be small compared to k_BT. This is because of the apparent moiety mismatches in comparison to the idealized picture above, and is borne out by experiment [5–7].

In this study we examine a very different dopant, di(4PPB5)3Si (Fig. 3), which by itself has been shown to have a Sm-C_A^* phase [10]. Unlike the P7-PIMB dopant, this molecule has a rather flexible bent-core that contains a silane group, and whose core dimension is comparable to that of the flexible part of the smectic layer. Although the silane core tends to mix poorly with both alkanes and aromatic rigid rods, it still is expected to mix better with the flexible part of the TFMHPOBC molecules, while the rigid-rod segments should mix better with the rigid parts of the smectic. Additionally, and unlike P7-PIMB, the legs of di(4PPB5)3Si do not terminate in long alkyl groups. Thus di(4PPB5)3Si, excepting that the core is somewhat flexible, also approximates the idealized dopant discussed above, and also would be expected to have an appreciable value of $u_{di(4PPB5)3\ Si}$, although significantly less than the thermal energy per dopant molecule.

In order to test these ideas we have examined the behavior of the field-induced anticlinic to synclinic phase transition for the low rigidity bent-core dopant di(4PPB5)3Si dissolved in TFMHPOBC. Although we found that the interaction coefficient per bimesogen $u_{di(4PPB5)3\ Si} < u_{P\text{-}7PIMB}$, it is not *much* smaller. This result indicates the importance of the structure of the bimesogen and bent-core molecules on the proclivity of the mixture to form an anticlinic phase.

Five liquid crystal mixtures were formulated. First, a single batch of TFMHPOBC having enantiomer excess $X=0.2$ was prepared, where $X \equiv ([R]-[S])/([R]+[S])$ and where $[R]$ and $[S]$ denote the mole fractions of right-handed and left-handed enantiomer. From this initial batch, five samples were made by dissolving the bimesogen di(4PPB5)3Si into the TFMHPOBC matrix. The final mixtures had bimesogen concentrations $C=0$, 2, 4, 5, and 6 wt %, each with an uncertainty of ±0.1wt %. Cells were prepared using two indium-tin-oxide-coated glass slides, which were cleaned and then spin-coated with the polyamic acid RN-1175 (Nissan Chemical Industries). The slides were baked at 250 °C for 1 h and then rubbed with a cotton cloth affixed to a rubbing machine. The slides were placed together, separated by strips of Mylar of nominal spacing 2 or 5 μm, and cemented. The cells were placed in a temperature-controlled hot stage, which in turn was placed on a rotation stage, and the thickness d of each cell was determined by an interference technique. The thicknesses of the five cells were found to be $d=8.2$, 3.4, 6.2, 3.0, and 3.8 μm for the $C=0$, 2, 4, 5 , and 6 wt % samples, respectively; the uncertainty in d was ±0.1 μm. Cells then were filled at $T=130$ °C, corresponding to the isotropic phase of the liquid crystal mixtures, and cooled slowly to ensure good alignment through the Smectic-A and synclinic Sm-C^* phases, then into the anticlinic Sm-C_A^* phase. As discussed previously [7], the sample is unwound via surface stabilization, and helicity is not a concern.

While viewing the cell under a polarizing microscope, a 1 Hz monopolar square wave voltage was applied to the sample, with the voltage switching between 0 and V every half cycle. The amplitude V of the square wave was ramped slowly upward until fingerlike solitary waves of synclinic phase invading the anticlinic were observed, and the threshold voltage V_{th} was recorded; the threshold field $E_{th}=V_{th}/d$. Measurements at each bimesogen concentration C were made as a function of temperature on cooling, and the resulting phase diagram T vs E is shown in Fig. 4. The interaction coefficient $U=\frac{1}{2}PE_{th}$ [8], where P is the spontaneous polarization associated with the field-induced Sm-C^* phase. Be-

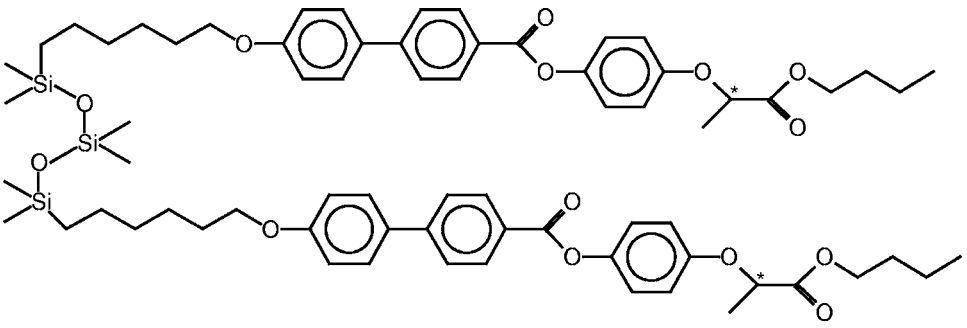

FIG. 3. Bimesogen di(4PPB5)3Si.

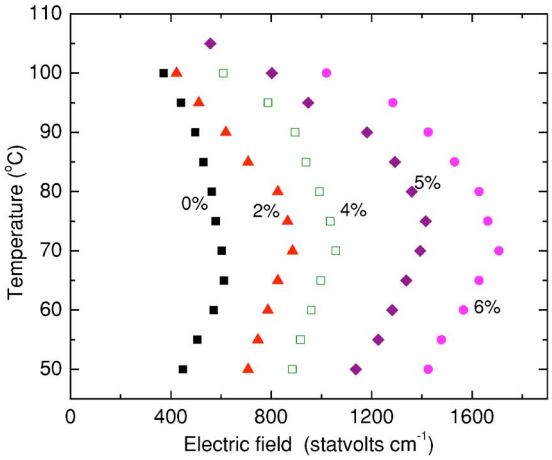

FIG. 4. (Color online) Electric field-temperature phase diagram at different concentrations C. For a given concentration C, the anticlinic phase is to the left of the curve and the synclinic phase is to the right of the curve. ■ corresponds to $C=0$ wt % di(4PPB5)3Si dopant, ▲ to $C=2$, □ to $C=4$, ◆ to $C=5$, and ● to $C=6$ wt %. The uncertainty δE_{th} in the threshold field is ±3%.

cause of the high switching voltages required for the two highest dopant concentrations C, two different procedures were used to determine P. For $C=0$, 2, and 4 wt % we used the ac bridge method [11] to determine directly P vs T. These results were compared with an indirect calculation for P that we had used earlier [7]. In that calculation we take P as a known function of θ and X only, and corrections to P due to the presence of the bimesogen dopant, which do not contribute to the polarization [5], are small. $P(\theta)$ for $X=0.2$ was obtained previously using data from Refs. [12,13], and is shown in Fig. 5 of Ref. [7]. We then measured the polar tilt angle θ vs T for each bimesogen concentration C (Fig. 5) using the method in Ref. [7], and thereby parameterized P in terms of T for each concentration C. We remark that the apparent tilt angles for the pure di(4PPB5)3Si material in its Sm-C_A^* phase [10] are larger than those of the mixtures shown in Fig. 5, as the more ubiquitous TFMHPOBC molecules dominate the tilt behavior in the mixtures. Also note that it was necessary to extrapolate the higher temperature

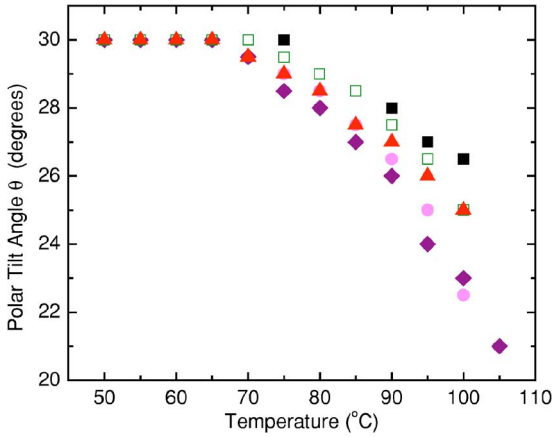

FIG. 5. (Color online) Tilt angle θ vs temperature. Symbols are same as in Fig. 4.

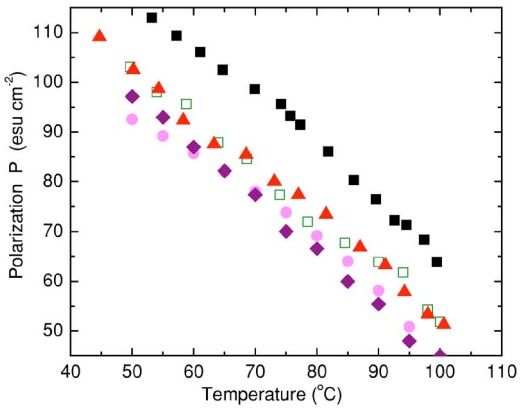

FIG. 6. (Color online) Polarization P vs temperature. Symbols are same as in Fig. 4.

$P(T)$ vs T data to the low temperature region ($T \lesssim 65\,^{\circ}$C, where θ saturates at approximately 30°). Using this method, excellent agreement for all temperatures was found between the direct measurements of polarization and the calculated values at bimesogen concentrations $C=0$, 2, and 4. In order to evaluate U at these lower concentrations we have chosen to use the *experimentally measured* values of P, which are shown in Fig. 6. On the other hand, for the two highest bimesogen concentrations we found that the large thereshold voltages and sample conductivity conspired to yield extremely noisy results for P. Thus, given the excellent agreement between experiment and calculated values for P at the lower concentrations, we have chosen to use the *calculated* values of $P(T)$ at $C=5$ and 6 wt %; these data are included in Fig. 6. We then use these values of $P(T)$, along with the results for $E_{th}(T)$, to determine $U(T)=\frac{1}{2}PE_{th}$ as a function of temperature and dopant concentration; the results are shown in Fig. 7. From the data in Figs. 5 and 7 we can plot U vs θ, which is shown in Fig. 8.

As expected, the data in Fig. 4 indicate that the presence of the bimesogen dopant increases the stability of the anticlinic phase [5,7]. Additionally, the absence of anomalous behavior for higher concentrations at the reentrant transition (lower temperatures) indicates that the bimesogen is not un-

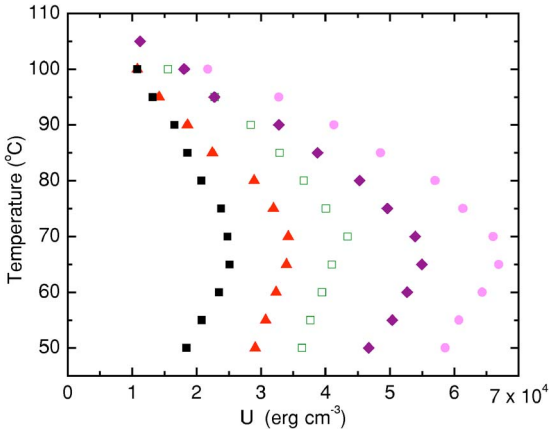

FIG. 7. (Color online) Interaction coefficient U vs temperature. See Fig. 4 caption for symbols.

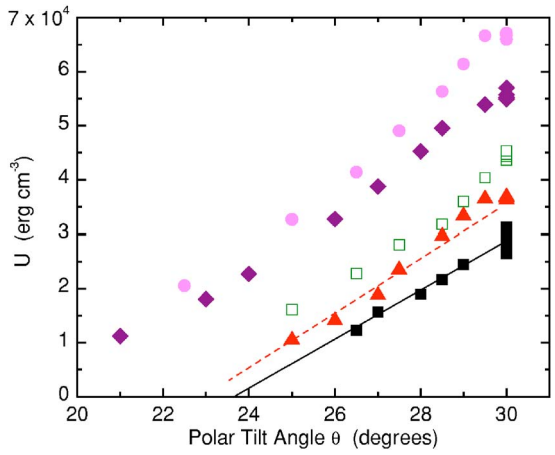

FIG. 8. (Color online) Interaction coefficient U vs polar tilt angle θ. See Fig. 4 caption for symbols.

dergoing an orientational transition, as was observed for the rigid bent-core mesogen P-7PIMB [7]. The absence of this orientation transition clearly indicates better packing with the host TFMHPOBC than for P7-PIMB in TFMHPOBC. Turning to Fig. 8, we see that for each concentration C, the interaction coefficient U increases with θ until tilt angle saturation occurs at $\theta \approx 30°$. This is qualitatively similar to the results for the bent-core dopant P-7PIMB [7], although for the P-7PIMB the energy U was found to be slightly more linear in θ than the results shown for the flexible bimesogen di(4PPB5)3Si. As in Ref. [7], we consider a linear extrapolation of the $C=0$ data to $U=0$ at $\theta \approx 23.5°$ (solid line in Fig. 8). At this angle θ the extrapolated values of U for $C>0$ are nonzero, and can be attributed to the presence of the bimesogen dopant. Unlike the extrapolated results for the bent-core molecule, it is difficult to obtain precise values for U when extrapolated to $\theta=23.5°$ because of the apparent curvature of U vs θ. Nevertheless, a reasonable value $U=(4\pm2)\times10^3$ erg cm^{-3} can be assumed for $C=2$ wt % case. Let us compare the contribution to U from the bimesogen dopant to the contribution from pairs of TFMHPOBC molecules in adjacent layers. Using the molecular weights 1020 for the di(4PPB5)3Si dopant and 612 for the TFMHPOBC, and assuming a mass density $\rho \approx 1$ g cm^{-3}, we find from $U=4\times10^3$ erg cm^{-3} at $C=2$ wt % (when extrapolated to $\theta=23.5°$) that the interaction coefficient associated with the addition of one flexible bent-core molecule is $u_{di(4PPB5)3Si}=3.5\times10^{-16}$ erg. This is smaller than that of the rigid bent-core dopant P-7PIMB, for which $u_{P\text{-}7PIMB}=7\times10^{-16}$ erg, but still much larger than the coefficient $u_{TFMHPOBC}$ for a *pair* of TFMHPOBC molecules. Because $U=0$ when we extrapolate the data at $C=0$ (no dopant) to $\theta=23.5°$, we shall estimate $u_{TFMHPOBC}$ at the Sm-C^*-Sm-C_A^* transition temperature instead. Here $U=1.1\times10^4$ erg cm^{-3} (and $\theta=26.5°$) for $C=0$, and we find $u_{TFMHPOBC}=2.3\times10^{-17}$ erg, considerably smaller than both $u_{di(4PPB5)3Si}$ and $u_{P\text{-}7PIMB}$. Interestingly, the pure di(4PPB5)3Si material has been found to exhibit a bulk interaction coeffient $U\sim2.5$–4.5×10^5 erg cm^{-3} in its Sm-C_A^* phase [10], which corresponds to $u_{di(4PPB5)3Si}\sim4$–8×10^{-16} erg per molecule. This value is quite similar to the value obtained above when di(4PPB5)3Si was used as a dopant in TFMHPOBC. Such a comparison cannot be made with P7-PIMB, which by itself does not exhibit a Sm-C_A^* phase.

A comparison of the quantity u_{dopant} for the different mixtures clearly indicates that the rigid bent-core dopant P-7PIMB stabilizes the anticlinic phase more effectively than the floppy bimesogen di(4PPB5)3Si. The fact that these dopants, each of which differs to a greater or lesser extent from the idealized dopant that would most encourage anticlinic tendencies in a synclinic/anticlinic material, have moderately large and comparable values of u_{dopant}, suggests that many other bent dopants are likely to have this tendency as well. It also suggests that appropriately designed mesogens such as di(4PPB5)3Si, incorporating most of the aspects that these dopants share with the idealized dopant discussed above, can result in a very much larger anticlinic tendency—and even possess a Sm-C_A^* phase by itself. An anticlinic phase containing an appreciable amount of such specially designed molecules, provided it also has a large electrical polarization in each layer, may facilitate a relatively temperature-independent control of the synclinic-anticlinic transition as a function of electrical field. It could also result in a phase that has a moderately large dielectric constant and allows for a very high electrical energy storage density, which may have applications in areas such as supercapacitor technology.

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