Park et al. Reply

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Park et al. Reply: In the preceding Comment [1], the authors (GB) have raised issues that we address below:

1. The authors contend that not taking the molecular bend angle into consideration, which is defined as a molecular biaxiality in Ref. [2], leads one to obtain lower values of $\langle P_{200} \rangle$ in the uniaxial nematic ($N_u$) phase. While at first this seems like a cogent comment, there is a contradiction in that the bend angle does not reflect molecular biaxiality in calculations of the order parameters. To assert that, one must demonstrate that the bend angle is responsible for the $\gamma$ angle (see Fig. 1 in Ref. [3]) dependence of measured polarized Raman intensity, which is impossible when using a Raman probe with a uniaxial symmetry.

According to their logic on page 955 of Ref. [2], order parameters obtained by using a uniaxial Raman probe originating from only one of the arms should be different from those from both arms. To understand the consequence of ignoring the bend angle, we obtained $\langle P_{200} \rangle$ by using three different probes [one originating from only one of the arms ($N = N_u$) and two from both arms (COC as well as the phenyl stretching modes)] (see Fig. 1), and they are identical within experimental error. This result is reasonable, since the $N_u/N_{b}$ phase is nonpolar, such that both arms might have the same orientation distribution function, and the rotational freedom of molecules in the $N_u$ phase averages out the influence of the bent-core shape. This illustrates that the consideration of the molecular bend angle is not as crucial as GB believe it to be and indeed might yield misleading results.

2. Should the bend angle be critical as suggested in the Comment, the assumption of a temperature-independent bend angle would be inconsistent with the x-ray diffraction results in Ref. [4] which suggest that the bend angle is indeed temperature-dependent. In Fig. 9 of Ref. [4], the positional order correlation length and, consequently, the structure factor $S(q)$ are reported to be temperature-dependent. The separation between small angle peaks, however, changes by as much as 40°. This change can arise only from the form factor $f(q)$ that explicitly depends on the bend angle. Evidently, the bend angle changes drastically over this temperature range, implying that if consideration of the bend angle is critical, one must use a temperature-dependent bend angle to perform a realistic analysis.

3. While GB argue the order parameter(s) belonging to the $N_{b}$ phase should ideally vanish at the transition to the $N_u$ phase, the literature is replete with reports of experimentally measured small values of the order parameter in the disordered phase. This has been attributed to “pretransitional” and “field” effects. (a) Pretransitional increase in the smectic order parameter was reported in many experiments including the pioneering work of McMillan [5], where the smectic order parameter has a finite value in the $N$ phase and it is attributed to smectic order fluctuations. (b) Theories predict a special Landau point [6], splitting of a Landau point into two tricritical [7] points, and a triple [8] point on transition lines in the $N, N_u$, and $N_{b}$ phase diagrams of biaxial nematics. Their nature near these points is too complex to obtain sufficient information from the study of one or two members of a homologous series. It is quite possible that close to one such point, A131 may yield a finite value of the order parameter on the other side of the transition. (c) Melnik et al. [9] reported a phase shift (proportional to biaxiality) in the $N_b$ phase of a lyotropic system, whose magnitude depends on the applied magnetic field. Similarly, deGennes has shown [10] that small values of the order parameter in the isotropic phase are observable under the influence of external fields. In Raman experiments, the surfaces impose an orienting field on the order parameter fluctuations and may be responsible for nonzero values of $\langle P_{200} \rangle$.

It is unclear why the $\langle P_{200} \rangle$ data for C5-Ph-ODBP-Ph-OC12 in Fig. 1 of their Comment are not the same as in Ref. [4].

In summary, the experimental evidence that we have provided strongly suggests that not taking the bend angle into account is a valid assumption and the facts we present also establish that GB have not provided a sound argument for the use of a fixed (vs temperature-dependent) bend angle to analyze Raman scattering data. The quality of our fits suggests that a modified Occam’s razor criterion should be applied: Given two explanations, that which more accurately reproduces the theory should be given the greater weight.

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FIG. 1. Temperature dependence of $\langle P_{200} \rangle$ obtained from Raman bands corresponding to COC stretching (○), $N = N_u$ stretching (■), and phenyl stretching (▲).
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