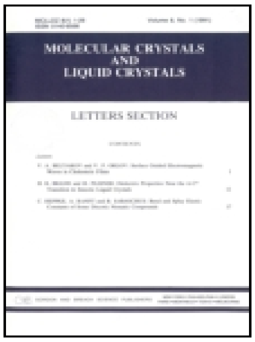

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Large Twist Elastic Constant in Diphenylacetylene-Core-Based Liquid Crystals

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We determine elastic constants K_{11}, K_{22}, *and* K_{33} *in two diphenylacetylene-core-based liquid crystals with azo and ester linkages. As we have already reported (Adv. Mater. (2014)* ***26****, 1918),* K_{33} *is extremely large (sub-nN) compared with* K_{11} *(pN) in the azo compound, since cybotactic smectic (Sm) clusters exist in whole the nematic (N) phase range. As a natural consequence,* K_{22} *is expected to be also large. We confirm that* K_{22} *is several tens pN, which is smaller than* K_{33} *but larger than* K_{11} *by one order of magnitude,* $K_{33} >> K_{22} >> K_{11}$*. This is the first compound, which has a larger* K_{22} *than* K_{11}*. In the ester compound, which has no clusters in the N phase, all the elastic constants are in a pN range, and are in the usual order,* $K_{33} > K_{11} > K_{22}$*. It is also important to note that not only* K_{33} *and* K_{22} *but also* K_{11} *show a pretransitional increase when the N-SmC phase transition temperature is approached.*

Keywords elastic constant; cybotactic cluster; pretransitional effect

1. Introduction

Elastic constants are one of the most important physical parameters for electro-optic device application of liquid crystals. At the same time they are also important from a basic science point of view. Elastic constants diverge with decreasing temperature in the nematic (N) phase when approaching the smectic (Sm) phase. This pretransitional phenomenon was observed quite long time ago in many compounds having the N-Sm phase transition [1–3] and the literatures were recently comprehensively summarized [4]. The phenomenon has also been theoretically studied since long time ago [5, 6]. However, most of the studies have been restricted in compounds with the N-SmA transition [1, 3], and there are very few reports in those with the N-SmC transition [2, 7, 8], partly because of a small number of compounds known. Theoretically, bend and twist elastic constants diverge at the N-SmA

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transition, and all the elastic constants including splay diverge at the N-SmC transition [5]. This is experimentally proved [1–3, 7, 8]. However, the relationship between three elastic constant values and the pretransitional phenomenon does depend on the molecular shape: Bent-shaped nematogens show small K_{33} [9–12], and even K_{11} of a T-shaped nematogen diverges when approaching the N-SmA transition temperature [13].

Recently, we found that one of newly synthesized diphenylacetylene-core-based liquid crystals has extremely large bend elastic constants K_{33} of sub nN [14]. Based on x-ray diffraction (XRD) measurements, we attributed this large K_{33} to the existence of Sm cybotactic clusters [14]. More recently, we measured K_{33} in analogues of diphenylacetylene-core-based compounds, and found K_{33} values vary over almost two orders of magnitude depending on a single linkage of these compounds [15]. In the present study, we measure K_{22} in two diphenylacetylene-core-based liquid crystals with azo and ester linkages. We found that K_{22} is larger than K_{11} and is of the order of several tens pN in the azo compound. In contrast, K_{33}, K_{11}, and K_{22} are in a pN range and are in this ascending order of magnitude in the ester compound, as well known in most nematogens [4, 7, 8] except for some nematogens with long alkyl chains [7]. These results indicate that K_{22} is also influenced by the existence of the cybotactic smectic clusters, as theoretically predicted [5], but the effect is not so large as K_{33}.

2. Experimental

Elastic constants were determined by observing the Freedericksz transition. For p-oxyAzo5 (p-oxyEster5), which has a positive (negative) dielectric anisotropy, K_{11} and K_{33} were obtained by measuring the capacitance change associated with the Freedericksz transition as a function of applied voltage using planar (homeotropic) cells; K_{11} (K_{33}) was directly determined by the threshold voltage and K_{33} (K_{11}) was obtained by the best fit of the experimental data with the theoretical expression [16]. Both compounds have the phase sequence of Iso-N-SmC. The cell thickness was 6.2 μm (3.5 μm), and the frequency of the applied electric field was 1 kHz. For K_{22} measurements, planar cells with comb electrodes (electrode separation of 10 μm) for in-plane field application were used [17, 18]. The cell thickness was 4.6–4.8 μm, and the off-set angles between the field direction and the rubbing direction were chosen by rubbing as 83 degrees for p-oxyAzo5 and 7 degrees for p-oxyEster5. The Freedericksz transition was observed by monitoring the transmittance between crossed polarizers and K_{22} was directly determined by the threshold voltage.

3. Results and Discussion

Let us first show K_{22} in p-oxyAzo5 in Fig. 1. The chemical structure of p-oxyAzo5 is also shown in Fig. 1. The previous results of K_{11} and K_{33} [14] are also shown by straight dotted and solid lines, respectively, since both elastic constants change almost linearly with temperature. We found that K_{22} also changes almost linearly with temperature. Unusually large K_{22} of several tens pN should be noticed. It is also important to note that this is the first compound, which has larger K_{22} than K_{11}. In our previous paper [14, 15], we concluded that Sm cybotactic clusters exist over the whole N phase range and are the reason why K_{33} shows extremely large values of sub-nN. The large K_{22}, although it is not so large as K_{33}, can be ascribed to the same reason, since not only the bend but also the twist deformations are not compatible with the smectic structure keeping the layer thickness unchanged. The smaller K_{22} compared with K_{33} may originate from a weaker influence of Sm clusters on

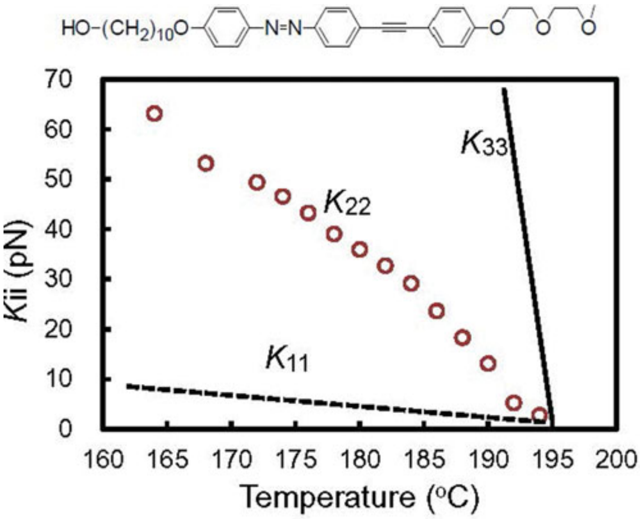

Figure 1. Temperature dependence of measured K_{22} values together with previously reported K_{11} (dotted line) and K_{33} (solid line) in p-oxyAzo5. The chemical structure is also shown at the top. Note that K_{22} is larger than K_{11}.

K_{22}. Actually, weaker divergent behavior in K_{22} than K_{33} was observed in the vicinity of the N-Sm phase transition temperature [19].

For comparison, we show the result of p-oxyEster5 (see Fig. 2). As shown in Fig. 2, the absolute values of K_{22}, K_{11}, and K_{33} are in a pN range and are in this order like conventional rod-shaped molecules [4, 8]. Important observation must be made in the divergent behavior;

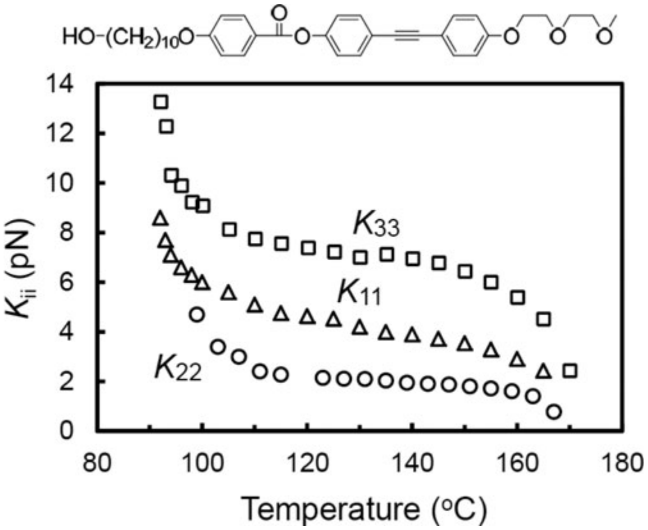

Figure 2. Temperature dependence of K_{11}, K_{22} and K_{33} values in p-oxyEster5. The chemical structure is also shown at the top. Note that not only K_{22} and K_{33} but also K_{11} divergently increase in the vicinity of the N-SmC transition.

not only K_{33} and K_{22} but also K_{11} divergently increase when approaching the N-Sm phase transition temperature. Normally, K_{11} does not show such a pretransitional behavior in compounds with the N-SmA phase sequence except for a few compounds [13, 16]. However, it was theoretically predicted [5] and experimentally confirmed [2, 7, 8] that compounds with the N-SmC phase sequence can also exhibit the pretransitional divergence of K_{11}. The present result adds another novel example exhibiting this behavior.

4. Conclusions

We conducted elastic constant measurements in two diphenylacetylene-core-based liquid crystals. Some important observations were made; (1) p-oxyAzo5 has large K_{22} of several tens pN, and is the first compound, that shows larger K_{22} than K_{11}, (2) in contrast, p-oxyEster5 has normal values of pN and order, $K_{22} < K_{11} < K_{33}$, and (3) the pretransitional increase of K_{11} is observed when approaching the N-SmC transition temperature in p-oxyEster5.

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