

Backbone orientational order in fatty acid monolayers at the air-water interface

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We report on the first observation of superlattice x-ray diffraction peaks (indicating herringbone ordering of the molecular cross sections) in a saturated fatty acid Langmuir monolayer. In the CS phase the “forbidden” (21) peak is observed with a resolution-limited width, implying that the herringbone order is long range. We also searched for this characteristic peak in the S , L_2 , L_2' , and L_2'' phases. Although each phase displayed some higher-order peaks, only the lowest-temperature (L_2'') phase showed the herringbone peak. These results do not preclude the existence of short-range herringbone order in the other phases; a Landau theory of lipid monolayers [V. M. Kaganer and E. B. Loginov, Phys. Rev. Lett. **71**, 2599 (1993)] predicts the existence of local herringbone order in some tilted phases, manifesting itself in the distortion of the molecular lattice from hexagonal. We have studied this distortion as a function of temperature along low-pressure isobars. The distortion goes to zero as the temperature is increased, but we do not see a first-order transition. [S1063-651X(98)13412-8]

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I. INTRODUCTION

Over the past ten years a fairly thorough understanding of the complicated phase diagram of fatty acid Langmuir monolayers has been arrived at by use of various experimental [1–13], theoretical [14], and computational [7,15] techniques. See Fig. 1 for a typical phase diagram, appropriate for monolayers of $\text{CH}_3(\text{CH}_2)_{19}\text{COOH}$ (heneicosanoic or “ C_{21} ” acid). The diagram also applies to all members of the homologous series from C_{14} acid to C_{24} acid when the temperature is adjusted $\sim 5\text{--}10^\circ\text{C}$ per CH_2 group [6] and the pressures are shifted very slightly. Although we know the basic lattice structures of the phases in this diagram [1], many questions remain to be answered. Some recent attention has been given to the question of whether there is ordering of the molecular backbones in any or all of the monolayer phases [1,7,14,15]. An infrared spectroscopy study of the CS phase (a two-dimensional crystal) indicated the presence of two molecules per unit cell, implying herringbone ordering [7]. Another low-temperature phase, L_2'' , is a tilted version of the CS phase and is also expected to have herringbone packing based on lattice energy calculations [8]. Although superlattice peaks implying herringbone order have been seen in x-ray diffraction experiments on a fatty *salt* monolayer [9], no such studies have been performed on the various phases of fatty acids. In an attempt to find direct evidence of long-range herringbone order in the various ordered phases of fatty acids, we have searched for “superlattice” diffraction peaks in these phases.

A Landau theory of fatty acid monolayers developed by Kaganer and Loginov [1(a),14] uses herringbone order parameters to successfully describe the nature and order of the known phase transitions. Their explanation requires that there be at least short-range herringbone order in three of the noncrystalline phases: the S phase, the L_2' phase, and a low-temperature section of the L_2 phase (which then becomes a separate phase, labeled L_{2h}). The high-temperature portion

of L_2 is then referred to as the L_{2d} phase, because the backbones are orientationally disordered. However, no unequivocal evidence of the phase transition from L_{2h} to L_{2d} exists [1(a),10]. Because the L_{2h} phase is a mesophase, the herringbone order if any is almost certainly short-range, and it is likely to be impossible to find direct evidence of such a transition through x-ray diffraction. For instance, there is no direct x-ray evidence that the R_I phase of bulk alkanes (equivalent to the S phase in monolayers) has herringbone order [1(b)], in spite of the fact that an IR spectroscopy study [15] indicates that short-range herringbone order is present. In the absence of direct proof, we may still look for indirect evidence that a herringbone to nonherringbone transition exists. Indirect x-ray evidence for herringbone order is found for both bulk alkanes and monolayers in the distortions of

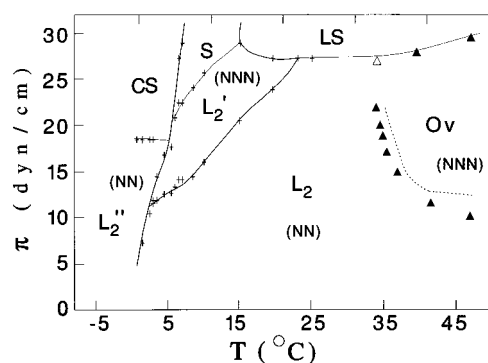


FIG. 1. Phase diagram for heneicosanoic (C_{21}) acid. Phases are labeled according to the notation of Ställberg-Stenhagen and Stenhagen [2], except for the R_{II} phase [3], and the Ov phase [4]. The crosses represent isotherm features, while the diamonds identifying the transitions to and from the Ov phase represent Brewster angle microscopy data taken from Ref. [5]. Heavy lines mark first-order transitions and thin lines mark second-order transitions. This phase diagram is roughly appropriate for any member of the homologous series of alkanolic acids (from C_{14} to C_{26} acid) if the temperature is adjusted by $\sim 5^\circ\text{C}$ per additional CH_2 group [6].

the lattice from hexagonal [1,7]. In an effort to observe the predicted transition between L_{2h} and L_{2d} phases, we have measured the lattice distortion as a function of temperature along two isobars using synchrotron x-ray diffraction.

II. EXPERIMENTAL DETAILS

Our experimental apparatus has been described in previous publications [11]. X-ray diffraction studies were performed at the Oak Ridge National Laboratory Beam Line X-14 of the National Synchrotron Light Source, Brookhaven National Laboratory. In order to decrease background scattering from the water, the beam (focused in the vertical direction) was incident at an angle of $\sim 1.9 \times 10^{-3}$ radians, which is just below the critical angle for total external reflection from water. The x-ray energy was 8.0 keV. The horizontal resolution was defined by vertical Soller slits in front of the detector and was $\sim 0.01 \text{ \AA}^{-1}$ full width at half-maximum (FWHM). The vertical resolution was set at $\sim 0.05 \text{ \AA}^{-1}$ (using Soller slits) for studies of lattice distortion in the tilted phases. When searching for higher-order and superlattice peaks, we removed the vertical Soller slits in order to increase count rates. The vertical resolution was then $\sim 0.2 \text{ \AA}^{-1}$. The subphase water was purified to 18 M Ω cm using a Barnstead Nanopure II system. The pH was adjusted to 2 using HCl in order to prevent any residual metal contaminants from interacting with the monolayer. The fatty acids (C_{19} , C_{20} , and C_{21} acids, stated purity $\sim 99\%$) were obtained from Sigma Chemical and dissolved in HPLC grade chloroform (stated purity 99.9+%) from Aldrich Chemical Company to form the spreading solution. All chemicals were used without further purification. A slight overpressure of helium was maintained in the trough to reduce radiation damage and air scattering.

III. RESULTS

A. Search for herringbone peaks

A plot of the diffracted intensity as a function of the in-plane wave-vector magnitude for the CS phase appears in Fig. 2. The wave vector K_{xy} cannot be separated into K_x and K_y components because the monolayers are powders in the plane. The intensity is plotted on a log scale so that the smaller peaks can be seen more easily. Because the basic structure is already quite well established, we scanned only around some expected peak locations. The presence of only two lower-order peaks, labeled (11) and (20), together with the higher-order peaks labeled (02) and (31), means that the lattice is centered orthorhombic, with two molecules per unit cell, and the labels indicate the indexing based on a rectangular nonprimitive unit cell. (These four peaks were first reported by Bohanon *et al.* [12].) This type of packing is also referred to as distorted hexagonal (DH) and applies to all of the phases we will discuss in this paper.

If the two molecules per unit cell were related by translational symmetry, the structure factor would be proportional to $1 + e^{i\pi(h+k)}$. This vanishes whenever $h+k$ is odd. Therefore our observation of the forbidden (21) peak means that the two molecules are not translationally equivalent. We also searched for but did not find the (01) peak, which also has odd $h+k$, and would appear at low K_{xy} , so that it should be

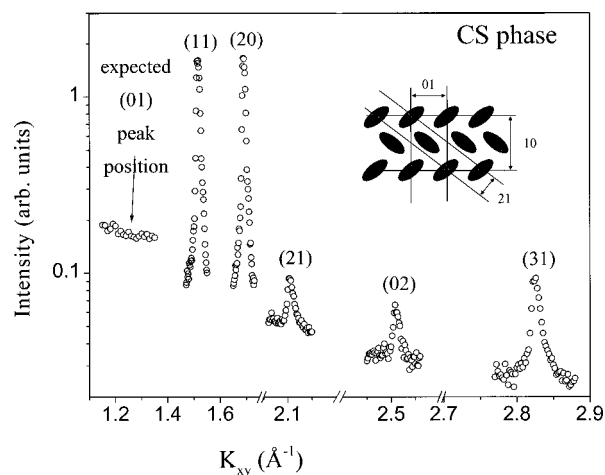


FIG. 2. Sample x-ray data (in the horizontal plane, i.e., at $K_z \approx 0$) from a C_{21} acid monolayer in the CS phase ($T = 7^\circ \text{C}$, $\pi = 30 \text{ dyn/cm}$). Peaks are indexed according to a centered orthorhombic lattice with two molecules per unit cell. The (21) peak at $K_{xy} = 2.09 \text{ \AA}^{-1}$ shows that there is a superlattice. The (01) peak is allowed in general for a two-molecule unit cell, but has zero intensity in a herringbone structure because the form factors for the two orientations are identical. The inset shows a centered orthorhombic lattice with herringbone packing. The intensities here and throughout the paper are plotted on a log scale in order to make the weaker peaks easier to see.

easy to see. However, as can be seen in the schematic diagram (Fig. 2), the two cross-section orientations in a herringbone structure are related by a reflection about the (01) direction, and so the two form factors are identical [9]. Thus the (01) has zero intensity in a herringbone structure. The (21) peak is not forbidden [it can be seen in the schematic diagram that the cross-section orientations are not symmetrical with respect to the (21) direction].

We did not search for the (10) peak, which also has zero intensity in a herringbone structure; nor did we look for the (12) peak, which is not forbidden but would appear at higher K_{xy} and so is presumably very weak. However, our observation of the (21) peak coupled with our failure to see a (10) peak leaves no reasonable hypothesis other than the existence of a herringbone arrangement of molecular cross sections. All peaks shown in Fig. 2, including the (21) peak, are resolution limited; thus the herringbone order in the CS phase is long range.

The CS phase occurs in a low-temperature and high-pressure region of the monolayer phase diagram. As the pressure is lowered, the distance between the head groups increases, but the tail groups still prefer to pack in the herringbone crystal bulk alkane structure. Permitting the molecules to tilt accommodates these two preferences. They tilt towards a nearest neighbor (NN) such that the packing in the plane that is perpendicular to the molecular cross sections (“perpendicular plane”) remains the same as for the CS phase. When molecules in a monolayer tilt away from the surface normal, some of the diffracted peaks will appear out of the water plane, depending on magnitude of tilt as well as the angle that the diffracted vector makes with the direction of molecular tilt. In the case of NN tilt we expect the (11), (02), (21), and (31) peaks to appear at $K_z \neq 0$. The (20) peak should remain at $K_z = 0$. Figure 3 shows diffraction from a

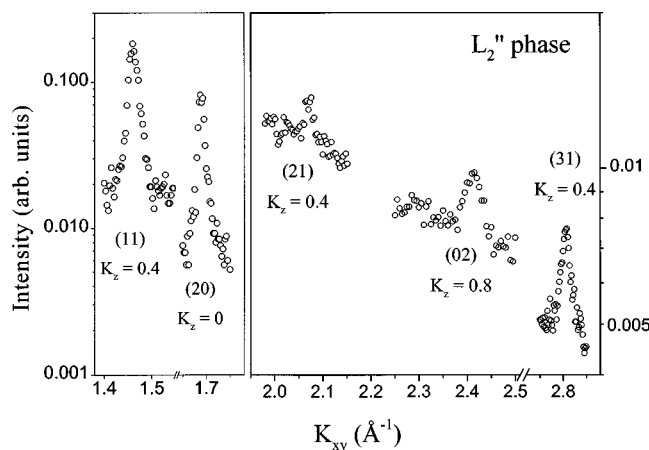


FIG. 3. Sample x-ray data from a C_{21} acid monolayer in the L_2'' phase ($T=3^\circ\text{C}$, $\pi=12\text{ dyn/cm}$). Peaks are indexed according to a centered orthorhombic lattice with two molecules per unit cell. The value of K_z at which each scan was taken is also indicated. The (21) peak at $K_{xy}=2.07\text{ \AA}^{-1}$, $K_z=0.4\text{ \AA}^{-1}$ implies that there is herringbone order in this phase as well. The higher angle peaks are plotted on a different scale, in order to make the smaller peaks easier to see.

monolayer in the L_2'' phase (which has NN tilt). Although our K_z resolution in these scans was poor ($\text{FWHM}\sim 0.2\text{ \AA}^{-1}$), we did observe that the appropriate L_2'' phase peaks were off plane, at approximately 0.4 \AA^{-1} for $k=1$ and 0.8 \AA^{-1} for $k=2$. Since in the perpendicular plane the structure is exactly the same as that of the CS phase, it is not surprising that we see the (21) peak in this phase as well (at $K_z\sim 0.4\text{ \AA}^{-1}$). See Ref. [1(b)] for a discussion of why a crystalline phase with tilt that varies as a function of pressure can exist in monolayers but not in bulk alkanes.

If the pressure is high (as in the CS phase) but the temperature is raised, the monolayer enters the S phase. A typical diffraction pattern observed from this phase is shown in Fig. 4. In contrast with Figs. 2 and 3 there is no intensity maximum at the expected position of the (21) peak. If broadening due to positional disorder were sufficient to wipe out the (21) peak, we would also expect it to wipe out the (02) and (31) peaks. As can be seen in Fig. 4, the (02) and (31)

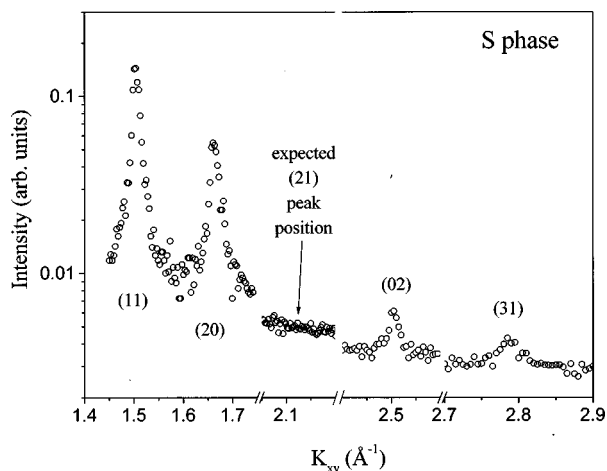


FIG. 4. Sample x-ray data (at $K_z\approx 0$) from a C_{21} acid monolayer in the S phase ($T=10^\circ\text{C}$, $\pi=30\text{ dyn/cm}$). There is no (21) peak, and hence no evidence of long-range herringbone order.

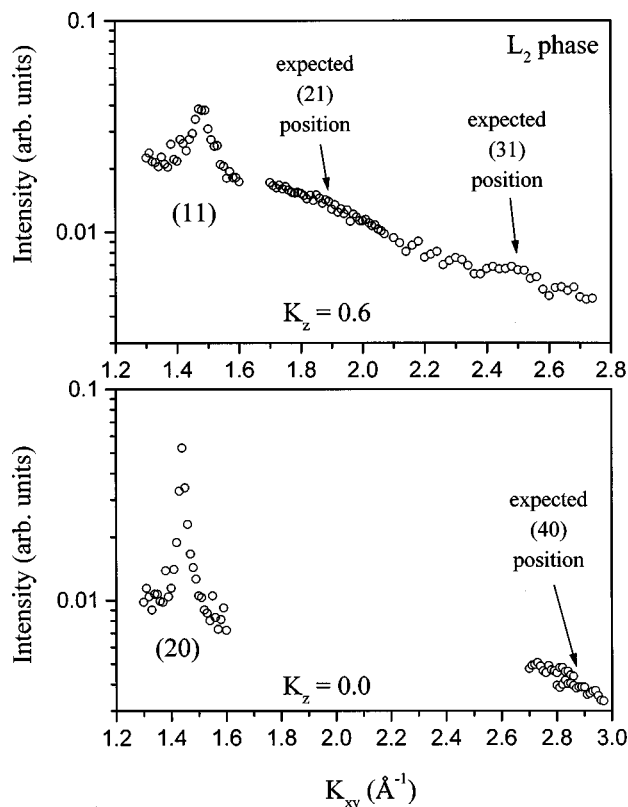


FIG. 5. Sample x-ray data (at $K_z\approx 0.6\text{ \AA}^{-1}$, top, and $K_z\approx 0\text{ \AA}^{-1}$, bottom) from a C_{21} acid monolayer in the L_2 phase ($T=5^\circ\text{C}$, $\pi=10\text{ dyn/cm}$). There are no higher-order peaks, indicating that there is significant disorder in this phase. The absence of a (21) peak at $K_{xy}=1.93\text{ \AA}^{-1}$, $K_z=0.6\text{ \AA}^{-1}$ indicates that there is no long-range herringbone order. We did not search for the (02) peak because it would occur at $K_z=1.2\text{ \AA}^{-1}$, which is outside the range of our apparatus.

peaks are still observed, though they are broader and weaker than their counterparts in the CS phase. We saw no evidence of a broad (21) peak. Thus there is no long-range herringbone order in this phase.

We also looked for the herringbone peak and other higher-order peaks in the tilted mesophases L_2 (Fig. 5) and L_2' (Fig. 6). Neither phase had a (21) peak. We observed no higher-order peaks in the L_2 phase, and only one higher-order peak in the L_2' phase. The position of the newly observed (02) peak (Fig. 6) is consistent with the indexing of the known (11) and (20) peaks. Two powder peaks are not enough to establish the structure of a two-dimensional lattice; thus the structure of the L_2' phase had only been assumed until now [11]. Our observation of a third peak that can be indexed on the basis of the assumed structure shows that the earlier assumption was correct. Because \vec{k}_{02} is perpendicular to the tilt direction, the (02) peak appears at $K_z=0$, where the background is low. This is probably why we see the (02) peak but not the (31) peak.

B. Isobar studies of distortion at higher temperatures

The absence of an observable (21) peak means that there is no long-range herringbone order in the S , L_2 , and L_2' phases; it does not mean that there is no short-range herring-

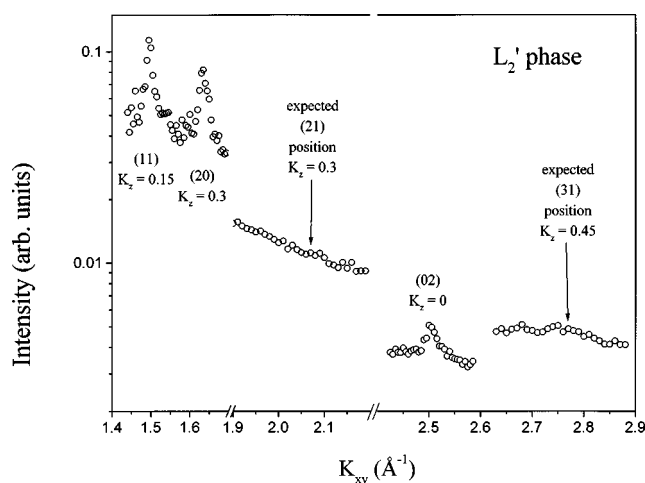


FIG. 6. Sample x-ray data from a C_{21} acid monolayer in the L_2' phase ($T=9^\circ\text{C}$, $\pi=22.5\text{ dyn/cm}$). There is no (21) peak, and hence no evidence of long-range herringbone order. The observation of an (02) peak confirms the centered-rectangular (DH) structure that until now has been assumed.

bone order. In Ref. [4], Sirota showed that the structure of the S phase is essentially the same as that of the R_I phase of bulk alkanes. An IR spectroscopy study [16] has shown that the R_I phase has short-range herringbone packing, and x-ray scattering studies are consistent with this picture [17].

We can use the lattice distortion to study the backbone orientational order in the low-pressure tilted mesophases L_2 , L_2' , and Ov . The primary distinction between the L_2 and L_2' phases is in the direction of the molecular tilt relative to the underlying lattice. The L_2 phase has NN tilt, while the L_2' phase has NNN tilt (tilt towards a next-nearest neighbor). Over a broad range of temperatures, a transition from L_2 to L_2' occurs as pressure is increased. At higher temperatures, the L_2 phase becomes favored, and the L_2' pressure range decreases until the phase disappears (see Fig. 1). As the temperature is increased further, there is a reentrance of the NNN tilt; this new phase is known as the Ov phase. The only difference between the Ov phase and the L_2' phase is that the molecules in the Ov phase pack into a hexagonal lattice in the perpendicular plane, while the molecules in the L_2' phase pack into a distorted hexagonal (DH) lattice. Because the tilt breaks the hexagonal symmetry, it is not clear whether the Ov phase can be considered as fundamentally different from the L_2' phase. Brewster angle microscopy studies of fatty acid/alcohol mixtures, which have contiguous Ov and L_2' regions, have been unable to identify a transition between the two [13]. Nonetheless, it appears that the Ov and L_2' regions are distinct in pure fatty acids. Furthermore, the Landau theory of Kaganer and Loginov [14] adequately explains the observed phase behavior of these four phases assuming that the Ov and L_2' phases have different backbone order. Their theory also requires that the L_2 phase be considered as two distinct phases, L_{2h} and L_{2d} , with the phase boundary being a continuation of the S - LS boundary and thus probably first order. We performed x-ray diffraction studies along two different isobars in order to attempt to distinguish a transition from backbone order to backbone disorder.

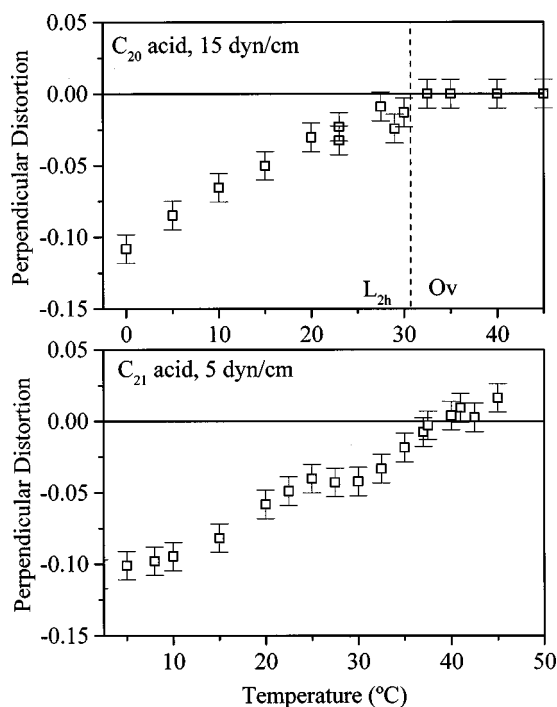


FIG. 7. Distortion in the plane perpendicular to the molecules as a function of temperature along two different isobars. Top: Data from C_{20} acid at 15 dyn/cm, which passes through the L_2 - Ov phase boundary at $T=30^\circ\text{C}$. Bottom: Data from C_{21} acid at 5 dyn/cm, which passes below the L_2 - Ov phase boundary at $T=35^\circ\text{C}$. Temperature axes are adjusted so that the two phase diagrams roughly overlap (given the 5°C shift appropriate for the addition of one CH_2 group [6]). The dashed line indicates the position of the L_2 - Ov phase boundary.

A good way to measure the distortion is to consider an ellipse drawn through the six nearest neighbors of a reference molecule [1(b)]. The difference between the major and minor axes of the ellipse will tend to zero as the lattice approaches hexagonal. Thus it is reasonable to define the distortion as $\xi=(l^2-m^2)/(l^2+m^2)$ where l and m are the major and minor axes. In the R_I phase, such distortion is taken as evidence that the molecules pack locally into a herringbone structure. The disorder in a herringbone pattern that might cause the odd $h+k$ peaks to be unobservable does not necessarily disrupt the lattice planes, so that the even $h+k$ peaks may be only slightly affected [1(b)].

Figure 7 shows plots of distortion in the perpendicular plane as a function of temperature at 5 dyn/cm and 15 dyn/cm. It is clear that the distortion tends to zero as the temperature is increased. We can divide the plot into two regions, at roughly $T=35^\circ\text{C}$ (for C_{21} acid). Above $T=35^\circ\text{C}$, we have $\xi\approx 0$, and below we have $\xi\neq 0$. The transition (if any) occurs at a temperature that is well above the location of the small peak intensity change reported by Peterson and co-workers [1(a),10]. The distortion appears to change continuously, within the (admittedly large) scatter of the data, although the theory in Ref. [9] requires a first-order transition.

There are several possible explanations for the lack of a first-order transition. Firstly, the transition occurs at significantly higher temperatures than the distorted-undistorted (S - LS) transition in untilted molecules. The distortion of the

ordered phase (a function of temperature) may decrease as the temperature increases to a value that is smaller than the scatter in our data. Sirota [1(b)] has suggested that the first-order $L_{2h} \rightarrow L_{2d}$ transition might be destroyed by weak interactions between the tilt order and the lattice distortion. This would be similar to the way in which the liquid crystal SmC \rightarrow SmI transition is destroyed by coupling between the bond-orientational and tilt order parameters [1(b),18]. Finally, Kaganer *et al.* [1(c)] have shown that the transition may be continuous even though the S - LS transition is first

order, if the sign of a fourth-order term in the Landau free energy changes sign.

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