Liquid-Crystalline Phase Behavior in a Zwitterionic Tetraazapentacene**

By Andrew E. Riley, Gregory W. Mitchell, Panayiotis A. Koutentis, Michael Bendikov, Piotr Kaszynki, Fred Wudl,* and Sarah H. Tolbert*

A 5,7-dioctadecylquinoloxalinophenazine zwitterion 1 has been investigated to determine its thermal phase behavior. A combination of differential scanning calorimetry (DSC), variable temperature low- and high-angle X-ray diffraction (XRD), and deuterium solid-state NMR spectroscopy were used to characterize the different phases of the tetraazapentacene 1. This molecule is found to exist in a variety of crystalline solid phases between room temperature and 167 °C, with different room-temperature phases resulting from crystallization from solution compared with cooling from the melt. Interestingly, the molecule exhibits liquid-crystalline behavior at high temperatures, between 167 °C and 186 °C, above which it becomes an isotropic fluid. The presence of liquid-crystalline behavior in a zwitterionic system opens up the potential for the use of these or related molecules in optoelectronic switching.

1. Introduction

Optically active dipolar fluids are the subject of significant current interest because of their potential applications in optoelectronic switching. Twisted nematic, cholesteric, various chiral smectic, and even achiral smectic liquid crystals have all been exploited for applications in devices.[1–9] These applications use dipolar molecules in which the domain structure can be modified using an external electric field. The field can be used to induce a macroscopic polarization, as in typical nematic and some smectic phases,[1] or it can be used to modify the orientation of already polar domains, as in ferroelectric smectic liquid crystals.[10–12] Changes in domain structure in turn modify the birefringence or the chirality of the fluid, which forms the basis for coupling an electrical signal with an optical response.[13–16] The magnitude of the overall coupling to the field is controlled, in part, by the size of the molecular dipoles on the constituent molecules. When liquid-crystalline molecules have a very large dipole moment, however, they tend to orient in an anti-parallel or antiferroelectric manner in the absence of an applied field.[17,18] The coupling between dipoles on the molecules thus prevents realignment with an external field if the field strength is below a threshold value. Above a threshold value, however, the dipole coupling is weaker than the coupling to the field and so molecules can be oriented by the field.[19,20] With a constant applied bias, some antiferroelectric liquid crystals can behave similarly to ferroelectric liquid crystals in terms of their ability to switch domain structure when a secondary field is applied.[21–23] These results indicate broad potential for interesting, field-dependent optical properties from anisotropic, dipolar fluids.

Our goal in this work is thus to explore the thermal properties of molecules with very large dipole moments (the limit being a zwitterionic species) and see if systems can be designed that show fluid or liquid-crystalline behavior in some temperature regimes. In designing a molecule to be liquid-crystalline, two main motifs are considered. There usually needs to be a rigid portion and some flexible substituents. The thermal motion of the flexible substituents contributes to the liquid like behavior, while the rigid portion of the material helps establish the anisotropic ordering of a liquid-crystalline phase.[5,24,25] To produce strong interactions with an applied field, a large permanent dipole also needs to be incorporated in the molecule. Of the two places to incorporate this functionality, the rigid section is the better choice because placing the dipole in the flexible section of the molecule could limit thermal motion and prevent liquid-crystalline behavior.[20] The net result is that the dipoles can be aligned in an anisotropic manner without thermal fluctuations completely disrupting the local order. This has the potential to give rise to liquid-crystalline behavior while maintaining the ability to interact with an external field.[20] Of course, as discussed above, for molecules with very large dipole moments, we expect anti-parallel dipole coupling between molecules in the absence of an applied field.

In previous work, we have shown that the tetraazapentacene family of heterocycles forms zwitterionic structures when syn aza-substituted, rather than a di-radical singlet ground state.[27]
The zwitterionic character of this family of compounds makes them promising candidates for field-based switching because of the large permanent dipole moment in the molecule—high-level calculations reveal that the calculated dipole moment of the tetraazapentacene molecule is 9.1 D.[28] In addition, the ability to control the structure through substitution can lead to a product with both an aliphatic region (flexible) and a ring system (rigid), which should promote liquid-crystalline behavior. For example, in recent monolayer studies, we have shown that when alkyl substituted molecules were spread onto a Langmuir trough, the tetraazapentacene zwitterion spontaneously formed striped domains that exhibit refractive index contrast when viewed through a Brewster angle microscope.[29] These stripes, which were a minority component of an otherwise featureless monolayer, exhibited a strong translational response to a static magnetic field.[30] Such domains could also be transferred to a solid substrate for further analysis. Analysis of full polarization-dependent second-harmonic generation (SHG) data was used to conclude that the domains corresponded to regions of homogeneous ferroelectric dipole orientation. From these observations we concluded that it is possible that the zwitterionic character of this family of compounds could make them interesting candidates for liquid crystal-based devices because of the large permanent dipole moment in the molecule.[28] We note that while none of the bulk phases produced by these molecules are chiral, the phases formed are non-cubic and non-centrosymmetric, and thus should show birefringence for at least some crystallographic orientations.

In this paper, we thus investigate the bulk phase behavior of a syn aza-substituted di-octadecyl tetraazapentacene zwitterion. While a variety of phases are observed with increasing temperature, the results shown below indicate that strong coupling between molecules results in significant in-plane correlations between molecules up to moderately high temperatures. To explore the high-temperature phase behavior in this system, we first use molecular modeling to calculate the expected structure of the individual molecules. Differential scanning calorimetry (DSC) is then used to determine the temperatures at which structural phase transitions occur. Low- and high-angle X-ray scattering are used in conjunction with deuterium quadrupolar solid-state NMR spectroscopy to obtain temperature-dependent structural information and to characterize molecular motion. The combination of these techniques provides the basis for a discussion of the phase behavior of the tetraazapentacene zwitterions as a function of temperature, as well as possible applications as liquid-crystalline materials.

2. Results

2.1. Quantum Mechanical Calculations

Since full optimization of a single molecule 1, using ab-initio or density functional theory (DFT) methods, is not feasible with modern computational power; we performed several model studies using molecular mechanics and semi-empirical levels of theory. Several minima were located for 1a at the PM3[33] level.

The ground-state configuration shows the two alkyl chains intertwined to maximize van der Waals interactions (Fig. 1a). In this conformation, the aromatic tetraazapentacene ring system is twisted. The more symmetric minima with an almost flat ring system and the alkyl chains in an all-trans configuration lies about 14.7 kcal/mol above the ground state (Fig. 1b). We note, however, that the intramolecular van der Waals attractive forces that stabilize the ground state are likely to be more important in the gas phase, where intermolecular interactions are negligible. To simulate a condensed-phase environment, where intermolecular interactions are likely to dominate the alkyl chain conformation, calculations are also carried out on a methyl-substituted derivative, 1c (see Scheme 1, Experimental). Because of the reduced molecular size, higher-level calculations could be performed on this molecule. B3LYP/6-31G* geometries were quite similar to those found at the PM3 level. For this system, the symmetric geometry shown in Figure 1b was found to be the ground state and a similar geometry is thus expected in the condensed phase.

The length of the molecule, defined as the distance from the hydrogen at the 13 position of 1a to a midpoint between the terminal carbons of the alkyl chains, is dependent on the conformation of the molecule. In the case where the aliphatic chains are twisted (Fig. 1a), the length is 26.0 Å, and where the chains are all-trans (Fig. 1b) the distance is 22.0 Å.[32]

2.2. Temperature-Dependent Structural Characterization.

In order to study the temperature-dependent structural properties of the tetraazapentacene zwitterion, calorimetry

Fig. 1. a) Conformation of 1a where the chains are intertwined. b) Conformation of 1a where the chains are “all-trans”. 
was used as a starting point to determine where phase transitions occur. A DSC trace of the tetraazapentacene is shown in Figure 2. The heating ramp shows several endotherms including a group at 121 °C, one at 167 °C, and one at 186 °C. The two highest-temperature transitions are reversible. The 167 °C transition shows no detectable hysteresis on cooling, whereas the highest temperature transition (186 °C) shows some hysteresis, especially at faster heating/cooling rates. The group of transitions around 121 °C is irreversible, with no corresponding transition during the cooling cycle. There is, however, a new exothermic feature in the cooling cycle below 57 °C. This new feature is reversible upon further heating and cooling cycles. The exact peak positions and integrated ΔH values are shown in Table 1. The DSC results suggest that there are at least three major phase changes that occur in the material upon heating and two distinct transitions, with the possibility of a third, more diffuse transition occurring during cooling. The question now is to determine the character of these phases and find out if any of them are liquid-crystalline in nature.

Table 1. Transition enthalpies and exact peak positions corresponding to the DSC traces shown in Figure 2.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Peak</th>
<th>Maximum</th>
<th>ΔH</th>
</tr>
</thead>
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<td>endo 1</td>
<td>122.0</td>
<td>45.5</td>
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<tr>
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<tr>
<td>heating</td>
<td>endo 3</td>
<td>185.8</td>
<td>28.8</td>
</tr>
<tr>
<td>cooling</td>
<td>exo 1</td>
<td>179.8</td>
<td>-27.9</td>
</tr>
<tr>
<td>cooling</td>
<td>exo 2</td>
<td>165.0</td>
<td>-20.2</td>
</tr>
</tbody>
</table>

Figure 3 shows temperature-dependent high-angle X-ray diffraction patterns for the tetraazapentacene. The starting phase (I) shows narrow peaks indicative of the atomic ordering of a crystal. Heating to immediately below the first DSC transition (121 °C) reveals little change in the high angle pattern (I). Above 121 °C (II), the high angle pattern still exhibits crystalline order. It is clear, however, that there has been a change in the periodicity of the material. The next interesting temperature regime is between the two sharp endotherms at 167 °C and 186 °C (III). This pattern has lost most of the crystalline order on the atomic scale and shows only broad features. Completing the heating ramp (T > 186 °C), pattern (IV) shows no high-angle order, which must correspond to an isotropic state. The last two patterns (II_2 and V) were obtained upon cooling of the sample after heating above the first transition (121 °C). Pattern (II_2) is obtained at 100 °C; the similarity between this and phase II emphasizes the irreversible nature of the 121 °C transition. The final pattern (V), collected at 30 °C, demonstrates that cooling to room temperature leads to the formation of a crystalline solid with different periodicity than the starting phase. From the high-angle X-ray diffraction data, we can conclude that the tetraazapentacene starts as a crystalline solid and undergoes one solid–solid phase transition to another crystalline solid. This is then followed by transitions to two liquid or poorly ordered phases. Upon cooling, the second crystalline phase is recovered, but a new phase is obtained upon full cooling to room temperature.

The high-angle diffraction is complimented by the low-angle X-ray scattering shown in Figure 4. The low-angle data provides information about the nanometer-scale order of the system. The first important result from the low angle-scattering is that all patterns show an evenly spaced lamellar progression, indicating that fundamentally these materials have a layered structure. Based on simple molecular considerations, it is likely that these layers are comprised of alternating rigid, aromatic moieties and floppy alkyl moieties. Careful examination of the data shows that there are three distinct lamellar patterns. The transitions between these patterns correspond well to transitions measured by DSC at 121 °C and 167 °C. The higher-tem-
perature transition (186 °C) is also accounted for—there is a drop in intensity around this temperature that indicates the formation of an isotropic phase. Consistent with these results, birefringent phases are observed using polarized optical microscopy (POM) at all temperatures below 180 °C. Unfortunately, no distinctive textures can be observed by POM in any of the anisotropic phases. It is likely that strong intermolecular interactions result in domain sizes too small to be observed by conventional light microscopy.

Figure 5 tracks the peak position of the fundamental diffraction peak (and thus the periodic repeat distance) for each of these layered structures. The graph also includes the peak positions for the cooling ramp, and a second cycle that demonstrates the reversibility of the low-temperature transition (57 °C). All of the transitions, with the exception of the last low-temperature one, show discontinuous jumps in peak position, indicative of first-order transitions. The transitions observed upon cooling also show good agreement with the DSC endotherms, although most of the transitions appear at slightly higher temperatures than those seen in the DSC. This difference in temperature is probably a result of errors in temperature calibration for the hot air stream used to heat the sample. Because melting transitions are used to calibrate the system, calibration can only be performed with increasing temperature, and thus some error is introduced upon cooling. The fundamental diffraction peak position for the cooling cycle has similar values for regions II and IIb, and regions III and IIIa. No region similar to phase I appears upon cooling. Similarly, region V (below the 57 °C transition observed in DSC) also has no analog in the first heating cycle. This region shows a gradual structural transition, in good agreement with the broad endotherm observed in the DSC. During the second and subsequent heating and cooling cycles, region V demonstrates a reversible structural transition to a value similar to regions II and IIb, which is also in agreement with the DSC data.

The information from Figure 5 can be used to calculate linear thermal expansion coefficients. These values, presented in Table 2, provide additional information about the nature of each phase. The linear expansion coefficient is defined as

$$\alpha = \frac{1}{d_{\text{lamellar}}} \left( \frac{\partial d_{\text{lamellar}}}{\partial T} \right) \rho$$

and corresponds to the fraction change in lamellar spacing with temperature. Generally speaking, crystalline solid phases have smaller α values than liquid-crystalline phases, and the smaller the value of α for a crystalline phase, the lower the degree of molecular motion. Accordingly, phase III, which shows no high-angle diffraction pattern, also has a very large value of α, typical of a liquid-crystalline phase. Phases I and II appear to be conventional solid phases and show fairly small values of α. The large α value observed for phase V may be, in part, the result of the slow transition and the fact that significant structural optimization is still occurring over the temperature region used to calculate the α value.

Deuterium solid-state NMR spectroscopy is used to verify our phase assignments for this material. This technique is sensitive to the motion of the carbon–deuterium bond.[33,34] The experiment makes use of the analog of the tetraazapentaene prepared per-deuterated at the carbon alpha to the nitrogen on the aliphatic tails (1b). As a static solid with little C–D motion, the quadrupolar coupling constant is expected to be ~168 kHz.[33,35] This value will decrease as the deuterium gains motional freedom.[36] Figure 6 shows the deuterium NMR
spectra at different temperatures. The inner splitting of the as-synthesized solid at room temperature is 120 kHz with a full width of twice that value (240 kHz). The inner splitting is equal to \(0.75 \omega_Q\), where \(\omega_Q\) is the quadrupolar coupling constant. Quadrupolar coupling constants obtained at a range of temperatures are presented in Figure 6. The quadrupolar coupling constant of 160 obtained at room temperature is indicative of a typical static solid.\[^{35}\] The splitting does not vary significantly until after the second DSC transition, indicating that all phases observed up to 167 °C are normal solid phases. The small changes in the deuterium splitting leading up to the second transition can be attributed to thermal vibrations and librations.

At the second transition, the peak shape changes from a typical power pattern to something indicative of a partially aligned liquid crystal (Fig. 6).\[^{34}\] The intense ‘horns’ and weaker ‘shoulders’ are replaced by a plateau which results from a gain in intensity of the ‘shoulder’ and a loss in intensity from the ‘horns’ as the liquid-crystalline domains align with the applied magnetic field.\[^{34,36}\] This intensity change corresponds to increased alignment of the lamellar domain directors parallel to the applied field. Such domain director alignment corresponds to lamellar layers oriented perpendicular to the field direction and thus to pentacene planes oriented parallel to the applied field.\[^{36}\] This orientation minimizes magnetic field-induced ring currents in the conjugated pentacene ring system and is thus the expected orientational ground state of a lamellar liquid-crystal phases based on an alkyl-substituted pentacene ring system in an applied magnetic field.\[^{36}\] By correlating the full width of the \(^3\)H NMR spectrum with the outer shoulders of a typical powder pattern, a quadrupolar coupling constant of 67 kHz can be deduced. This value is significantly less than the static value of 160 kHz, indicative of significant motion in the high-temperature lamellar phase obtained above 167 °C. This fact, together with the observation of facile orientation of the lamellar domains with the applied magnetic field provide strong evidence for the formation of a liquid-crystalline phase. The results are further confirmed by additional two-dimensional low-angle X-ray diffraction studies (not shown) which indicate that a change in lamellar domain orientation due to surface alignment can be observed upon transition to the highest-temperature lamellar phase at 167 °C. All results thus confirm the fluidity of the high-temperature lamellar liquid-crystal phase.

After long heating times, the aligned liquid crystal also shows the growth of a narrow central peak. This peak, which is attributed to thermal degradation, shows a narrow splitting of its own in the phase III range (\(\omega_Q = 0.5\) kHz), and is thus thought to be intercalated deuterated alkane that is thermally eliminated from the material. After the highest temperature transition, the material becomes completely isotropic and a single peak pattern is observed. The \(^3\)H NMR spectroscopy thus suggests that the material remains solid up to ~170 °C, becomes liquid-crystalline after this point, and finally becomes an isotropic liquid at higher temperatures. Cooling below 178 °C regenerates a static powder pattern with a quadrupolar coupling constant of 155 kHz, indicating that the material reforms into a normal solid phase upon cooling from the liquid-crystalline regime.

An interesting complication occurs while taking the solid-state NMR spectrum. For some samples, electron spin resonance (ESR) measurements indicate the presence of very small amounts of paramagnetic impurities. This type of impurity can significantly affect NMR spectroscopy for coupled systems. While the intensity reduction caused by the radicals could not be measured for a solution-phase sample, even very small ESR signals correlate with dramatic changes in the solid-state NMR signal, suggesting a highly coupled π-ring system in the solid phases.

### 3. Discussion

The different pieces of data provide information about the thermal phase behavior of the tetraazapentacene. It starts as a crystalline solid with an overall layered architecture. After the group of transitions at 121 °C, the material is still a solid that retains its layered structure, but with different atomic ordering as evidenced by changes in X-ray diffraction. The phase transition at 167 °C corresponds to a solid to liquid-crystalline phase transition, as indicated by the retention of the nanoscale layered structure but the loss of sharp peaks corresponding to atomic scale order. This conclusion is further supported by the large decrease in the width of the \(^3\)H NMR pattern above...
167 °C. The final portion of the heating ramp corresponds to the formation of an isotropic phase above 186 °C, as evidenced by the loss of both low-angle and high-angle diffraction peaks in the scattering data and the isotropic nature of the deuterium NMR signal.

The cooling cycle revisits the liquid-crystalline phase, and then returns to a solid phase below 167 °C. The similarity of the 2H NMR splitting at 150 °C and 100 °C indicates that this is a conventional solid phase with little change in the degree of molecular motion observed across the range of thermal stability. Note that the deuterium coupling constant for phase II (155–156 kHz) compared to phase I (160 kHz) correlates well with the measured thermal expansion coefficients for these phases. A somewhat large $\alpha$ is obtained for phase II, compared to phase I, consistent with slightly increased tail motion in the higher temperature phase and a lower $\omega_N$ value. The final transition occurs at 57 °C, and based on both diffraction and 2H NMR, this gradual transition is a crystalline-to-crystalline solid–solid phase transition. The gradual nature of the transition may be related to the fact that it occurs at fairly low temperature and could be kinetically frustrated. The fact that the phase does not form during solution crystallization might support the hypothesis of kinetic frustration. Alternatively, the almost perfect reversibility observed in the diffraction peak position upon second cycle heating and cooling (Fig. 5) suggests that this transition might be second order in nature and thus the gradual change could be intrinsic.

While liquid-crystalline behavior is only observed over a fairly small temperature range (and not at room temperature), the presence of liquid-crystalline material indicates that our molecular design template is a valid approach. The lamellar architecture of all phases is also anticipated based on molecular geometry. Anti-parallel alignment of the head groups should satisfy the electrostatic interactions of the molecules and establish the lamellar nature of the molecular packing in the bulk phases. The wide range of available packing possibilities for the aliphatic tails produces the range of solid phases observed upon heating and cooling, and ultimately leads to the liquid-crystalline behavior observed at high temperatures.

Using molecular modeling as a basis for the size and geometry of a single molecule at low temperature, we can begin to postulate about the possible chain-packing patterns that produce each of the phases indicated in Figure 5. We note that, theoretically, these packings could be determined exactly from the high-angle powder diffraction shown in Figure 3. Unfortunately, the quality of these patterns is not sufficient for Reitveld refinement, and high-quality single crystals of these materials have not yet been produced. As a result, we will simply use the lamellar repeat distance to speculate about compatible tail geometries. Figure 7 illustrates some possible modes of stacking. Table 3 contains the average repeat distance determined from small-angle X-ray scattering for each of the phases. If the tails retained the zero-temperature splayed conformation illustrated in Figure 1b (with the alkyl chains each 30° from the plane of the ring system) and the alkyl chains completely interdigitated, the lamellar stacking distance would correspond to around 22.0 Å. This is well within experimental error of the final $d$-spacing (~22.9 Å, phase V) observed upon cooling. Phase V shows the smallest repeat distance measured in this system and this phase is always obtained upon cooling the pure solid. This result indicates that the interdigitated and splayed structure is probably the stable geometry for the alkane tails at low temperature.

Larger $d$-spacings can be attributed to alternate packing of the alkane tails. For example, the material starts at a rather large $d$-spacing (region I), which is probably a kinetic phase resulting from the solution-phase crystallization conditions. The actual distance of 28.0 Å can be interpreted as tails that are only slightly interdigitated, or more likely, as tails that do not obtain the calculated molecular geometry and thus lie closer to the plane of the aromatic rings. Even with a tail geometry that is closer to coplanar with the ring system, the model’s prediction of a 26.0 Å axial length indicates that the alkane chains are only partially interdigitated.

Upon heating to 120 °C, a phase transition to phase II occurs. Based on 2H NMR and a combination of low- and high-angle X-ray scattering, we believe regions II and II$_D$ correspond to the same phase. The source of the small differences in lamellar spacing between phase II and II$_D$ is not obvious (for example, the average interlayer spacings are 26.0 Å and 25.1 Å, respectively). The differences may relate to the formation of some impurities at high temperature caused by sample degradation. This is supported by second heating cycle data, where the sample is heated only past the first transition (see Fig. 5). For this experiment, the interlayer spacing is close to the value ob-

![Fig. 7. Cartoon of possible packings for the different phase regions shown in Figure 5. The rectangular section indicates the tetrazapentacene ring system. Straight lines emanating from the rings indicate rigid aliphatic chains, while wavy lines indicate thermal disorder. Splayed chains are not actually splayed in the plane of the aromatic ring (as shown), but rather should be displaced into and out of the plane of the page (as shown in Fig. 1b). Parallel chains indicate a geometry similar to that shown in Figure 1a.](http://www.afm-journal.de)

<table>
<thead>
<tr>
<th>Region</th>
<th>Spacing [Å]</th>
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<tbody>
<tr>
<td>I</td>
<td>28.0</td>
</tr>
<tr>
<td>II</td>
<td>26.0</td>
</tr>
<tr>
<td>III</td>
<td>27.9</td>
</tr>
<tr>
<td>III$_D$</td>
<td>27.3</td>
</tr>
<tr>
<td>II$_D$</td>
<td>25.1</td>
</tr>
<tr>
<td>V</td>
<td>22.9</td>
</tr>
</tbody>
</table>
tained for phase II upon increasing temperature (25.5 Å), probably indicating less sample degradation because the sample experiences lower overall temperatures. The reduced repeat distance for phase II (26.0 Å) compared to phase I (28.0 Å) probably corresponds to increased interdigitation of the aliphatic tails or a change in tail angle to approach the ground-state geometry in which the chains are splayed significantly out of the plane of the aromatic rings.

Regions III and III′ are believed to correspond to liquid-crystalline behavior, which requires significant tail disorder. In agreement with this, the lamellar repeat distance is fairly long (27.9 Å and 27.3 Å average repeat distance for region III and III′ respectively). Theoretically, the length of an alkane chain in a lamellar liquid-crystal phase should be about 0.7 times the length of the rigid chains. Depending on the degree of interdigitation, this could produce lamellar spacings between 19 and 34 Å. The measured value near to 27–28 Å indicates that the chains are mostly non-interdigitated, which is typical of liquid-crystalline materials. The large thermal expansion coefficient observed for these phases (Table 2) correlates directly with increased molecular motions observed in 2H NMR (Table 4) and the large interlayer spacing seen in low-angle X-ray scattering (27.3–27.9 Å, Fig. 5). Region IV corresponds to a true liquid phase in which the lamellar ordering is finally lost.

Table 4. 2H NMR quadrupolar coupling constants obtained at various temperatures. The roman numerals correspond to the temperature regions shown in Figure 5. The subscript d corresponds to data collected upon cooling.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature [°C]</th>
<th>Quadrupolar coupling constant [kHz]</th>
</tr>
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<tr>
<td>I</td>
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<td>160</td>
</tr>
<tr>
<td>II</td>
<td>160</td>
<td>155</td>
</tr>
<tr>
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<tr>
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<tr>
<td>III′</td>
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</tr>
<tr>
<td>V</td>
<td>30</td>
<td>160</td>
</tr>
</tbody>
</table>

We can begin to understand the molecular motions allowed in the liquid-crystalline phase in more detail by examining the 2H NMR results. Motion of the entire molecule, or rotation about the N–C bond joining the tail to the aromatic plane will all change the angle of C–D bond with respect to the applied field. If these motions occur rapidly on the NMR time scale, they can make different deuterium orientations effectively equivalent, resulting in narrowing of the NMR powder pattern. For the solid phases, vibrational motion can also induce some decrease in the apparent quadrupolar coupling constant, but the effects are generally small. In agreement with this idea, all solid phases of the tetraazapentacene observed in this work show quadrupolar coupling constants between 155 and 160 kHz.

At the solid-to-liquid crystal transition, a large decrease in the quadrupolar coupling constant occurs (from ~160 kHz down to ~67 kHz). This decrease can be modeled by examining the types of molecular motions that should be allowed in the liquid-crystalline phase. If the tails are able to rotate freely, this will make the two deuterium atoms on each tail equivalent and decrease the quadrupolar coupling constant by a factor of two. The roughly two-fold decrease in quadrupolar coupling constant suggests that the phase transition from solid to liquid crystal corresponds mostly to tail melting. This relatively constrained motion of the liquid crystal is perhaps expected based on the strong coupling between the zwitterionic head groups. We note that the decrease in νQ is actually somewhat greater than two-fold, however, a fact that indicates some increased motion of the entire molecule, as well as chain melting upon transition to the liquid crystal phase. This conclusion is supported by the observation of field-induced alignment of the liquid-crystal phase. The breadth of the 2H NMR pattern, however, indicates that this molecular motion is fairly slow on the NMR time scale.

4. Conclusion

Alkyl-substituted tetraazapentacenes present a unique system because they are zwitterionic, yet have an overall molecular structure that promotes a range of possible packing configurations. The presence of strong dipole coupling between ring systems on neighboring molecules and a flexible region that is thermally influenced produces interesting and complex thermal phase behavior. A range of experimental techniques indicates that, at lower temperatures, the tetraazapentacene is a layered solid with a structure that probably optimizes strong dipole coupling between neighboring molecules. Despite this fact, at high temperature, thermal disorder in the alkane tails is able to compete with the dipole–dipole coupling, leading to a lamellar liquid crystal phase. At even higher temperature, an isotropic fluid phase is possible. The results demonstrate that a liquid-crystalline phase can be accessed if the structure of the molecule is tailored correctly.

Anisotropic dipolar fluids with large molecular dipoles are interesting systems for optoelectronic switching. Tetraazapentacenes, in particular, are an exciting system because of their zwitterionic character and thus their potential for strong coupling to an applied field. Unfortunately, the liquid-crystalline transition in this tetraazapentacene is at a higher temperature than the ideal operating range for almost any devices. By tailoring the structure of the tetraazapentacene, however, the phase behavior can potentially be tuned to bring the liquid-crystalline regime into a more useful temperature range. For example, longer alkane tails should increase thermally induced disorder and result in a lowered temperature for the liquid-crystalline transition. Unsaturation or heteroatom incorporation in the tails could also prevent optimal packing and lead to a lowered transition temperature. Finally, the addition of bulky groups to the aromatic ring system could be used to separate the zwitterionic rings and decrease the intermolecular dipole–dipole coupling. This should allow the thermal disordering of the aliphatic tails to dominate over the dipole–dipole coupling at a much lower temperature, while preserving the strong interactions with an applied field. Although the specific molecule examined here is not likely to have technological applications because of its high solid to liquid-crystalline transition temperature, the
presence of liquid-crystalline behavior in a zwitterionic tetraaza-
zapentacene opens up the potential for future advances.

5. Experimental

Temperature-Dependent Structural Characterization: Differential scanning calorimetry was performed using a Perkin Elmer (Pyris 1) instrument under N₂ atmo-
sphere. For all runs, the sample was rapidly heated from room temperature to 50°C. Once at 50°C, the temperature was increased at 10°C/min up to 195°C. All samples were then cooled back to 50°C, again at a rate of 10°C/min.

High- and low-angle X-ray scattering experiments were both performed using a Rigaku UltraX 18 rotating anode X-ray generator producing Mo Kα radiation. Diffraction patterns were collected using a Roper Scientific 1242×1156 cooled X-ray charge coupled device (CCD) detector. Temperature control was achieved using a feedback-controlled air stream that has been described elsewhere [40,41].

Two sets of variable temperature data were collected. For the high-angle data presented in Figure 3, the samples were heated at a rate of 10°C/min. At each temperature point shown in Figure 3, data were collected during a 10 min hold at the stated temperature. For low-angle scattering, patterns were collected in 1 min exposure times during a continuous ramp of 1°C/min. The temperature difference between the thermocouple and the sample was calibrated using a 3°-point linear correction based on the melting points of sulfur (mp = 117°C), ascor-
bic acid (mp = 190°C), and room temperature.

Molecular motion was probed using solid-state ¹H NMR spectroscopy. A ver-
tion of the tetrazapentacene that was deuterated on the alpha-carbon of the aliphatic tail was synthesized and used for the NMR measurements with a Bruker Avance 300 (7.05 T field) spectrometer. Data were collected using a standard quadrupolar echo pulse program with a 2.1 μs π/2 pulse, 50 μs and 42 ms dead-
time delays, and a 3 μs recycle delay [42]. All samples were flame-sealed in glass NMR tubes under a reduced-pressure argon atmosphere. Heating made use of the Bruker BVT500 forced-air VT system. The temperature inside the probe was calibrated using the chemical shift of 207PbSO₄.

Synthesis of the Alkyl-Substituted Tetrazapentacene Zwitterion: We have pre-
viously reported the synthesis of the bis-phényl substituted zwitterion, 5,7-di-
phenyl-5H,12H-quinoxalino[2,3-h]phenazine (diphenylisoquinolinedione, 5,7-DPPQO) [18]. The synthesis of 5,7-dioctadecyl-5H,12H-quinoxalino[2,3-h]phenazine (dioctadecylisoquinolinedione, 1) was similarly achieved, with a few minor modifica-
tions to improve yields (Scheme 1). Unlike N-phenyl-1,2-diaminobenzene, N-oct-
daetyl-1,2-diaminobenzene was not commercially available. Preparation was achieved by reaction of n-octadecylamine with 1-fluoro-2-nitrobenzene, followed by palladium-catalyzed hydrogenation.

General: The fluoronitrobenzenes were purchased from Lancaster合成 and used without further purification. Amines and amides were purchased from Aldrich Chemical Co. and stored in a dessicator. Palladium on carbon was like-
wise purchased from Aldrich Chemical Co. and stored under nitrogen. ¹H NMR spectra were measured on Bruker AMX 400 and Avance 500 machines. The IR spectra were obtained using a Mattson Infinity IIa spectrometer with a diffuse re-
fectance infrared Fourier transform (DRIFT) accessory from PIKE Technologi-
s, on a diamond ir. Melting points were obtained using a Mel-Temp from Laboratory Devices and are uncorrected. High-resolution electron impact mass spectra (EI-MS) (70 eV) were recorded on a triple sector instrument (VG/ MicroMass Autospec) tuned to 8000 static resolution (M/AM, 10% valley) using per-
fluorinated kerosine (formula weight 705, Lancaster Synthesis Inc.) for internal calibration. High-resolution fast-atom bombardment (FAB) mass spectra were taken using a positive ion VG-ZA mass spectrometer on a 3-nitrobenzal alcohol matrix. Matrix-assisted laser desorption ionization (MALDI) MS were recorded using a dihydroxybenzoic acid matrix on an Applied Biosystems DE-STR MAL-
DI-TOF instrument in reflection mode using external calibration.

N-Octadecylamine d₂ 2b: Octadecylamine (85% technical grade) was recrys-
tallized from MeOH to afford white needles, and was used without further purifi-
cation. A three-neck round-bottomed flask was charged with lithium aluminum deuteride (2.0 g, 47.6 mmol) and tetrahydrofuran (THF) (100 mL) distilled over sodium. The mixture was then cooled to -5°C. To the stirred suspension, octade-
cylation (8.0 g, 28 mmol), dissolved in THF (200 mL), was added dropwise. Fol-
lowering the addition of the solution to precipitate as a yellow solid. The organic materials were extracted with Et₂O, which was washed three times with a dilute hydrogen chloride aque-
ous solution. The ether layer was dried with magnesium sulfate and evaporated to dryness to give a yellow-orange solid. The solid was dissolved in boiling CHCl₃, which was slowly replaced by hot EtOH. Precipitation afforded the title compound (32.1 g, 95%) as a yellow solid, mp 46–49°C (DRIFT) [cm⁻¹] 3384, 3107, 2959, 2924, 2851, 1616, 1567, 1475, 1438, 1416, 1387, 1352, 1215, 1152, 1120, 1072, 1037, 867, 774, 749, 729, and 515; δH (400 MHz; CDCl₃) 8.17 (1H, dd, ArH, J=8.6 Hz, J=1.1 Hz), 7.42 (1H, dd, ArH, J=8.6 Hz, J=6.8 Hz, J=1.5 Hz), 6.85 (1H, dd, ArH, J=8.6 Hz, J=1.1 Hz), 6.64 (1H, dd, ArH, J=6.8 Hz, J=1.5 Hz), 3.30 (2H, t, CH₂, J=7.3 Hz), 1.72 (2H, q, CH₂, J=7.3 Hz), 1.44 (2H, m, CH₂, J=1.3 Hz), 0.88 (4H, t, CH₂, J=6.9 Hz), δC (500 MHz; CDCl₃) 145.52, 136.03, 131.63, 126.79, 114.99, 113.66, 42.95, 31.81, 29.58, 29.55, 29.24, 29.40, 29.24, 29.19, 28.85, 26.96, 22.57, 13.99; m/z (FAB) 391 (Found: MH⁺, 391.3329. C₂₇H₅₂N₂O₂ requires MH⁺ 391.3329. N-Octadecyl-1,2-diaminobenzene d₂ 3b: Compound 3b was prepared ac-
cording to the procedure described for compound 3a (87%), mp 45–47°C (DRIFT) [cm⁻¹] 3387, 2952, 2925, 2907, 2864, 1618, 1596, 1509, 1438, 1417, 1374, 1357, 1331, 1262, 1235, 1172, 1155, 1334, 1074, 1042, 751, and 501; δH (400 MHz; CDCl₃) 8.16 (1H, dd, ArH, J=8.8 Hz, J=1.5 Hz), 8.04 (1H, bs, NH), 7.42 (1H, m, ArH), 6.83 (1H, dd, ArH, J=8.5 Hz, J=1.2 Hz), 6.63 (1H, m, ArH), 1.72 (2H, m, CH₂), 1.12 (6H, t, CH₂, J=6.7 Hz), δC (500 MHz; CDCl₃) 137.71, 134.02, 126.83, 114.83, 116.40, 111.80, 31.82, 29.59, 29.56, 29.52, 29.51, 29.40, 29.33, 29.27, 21.44, 12.84, 14.00; m/z (MALDI) 392 (Found: MH⁺, 392.3349. C₂₃D₃₂N₂O₂ requires MH⁺ 392.3349. N-Octadecyl-1,2-diaminobenzene 4a: EtOH (150 mL) was degassed by vigorously bubbling argon through the stirring liquid. A solution of 1-octadecyl-
amino-2-nitrobenzene 3a (30.7 g, 78.5 mmol) in dis-
tilled THF (400 mL) was added to the EtOH under a flow of argon. The system was purged with argon for approximately 5 min. Under a stream of argon, 10% palladium on carbon (5.0 g) was added to the stirred solu-
tion. The mixture was warmed to ca. 40°C, and hy-
drogen gas was bubbled through the solution using a 20-gauge needle. Initially orange, the solution became reddish as hydrogen was introduced to the system. A steady stream of hydrogen was supplied for 4 h, at which point the solution became colorless. After an ad-

Scheme 1. Synthetic route for the preparation of the isofluoriridines 1a and 1b.
differential under a hydrogen atmosphere, the solution was filtered over carbon to remove the palladium. The resulting EtOH/THF solution was colorless, and was evaporated to yield the title compound (27.6 g, 97%) as a light-pink solid, mp 52–54 °C (vapour: DRIFT [cm⁻¹] 3377, 3035, 3046, 2922, 2857, 1619, 1607, 1521, 1469, 1453, 1345, 1317, 1274, 1125, 1095, 739, and 722; δH (500 MHz, CDCl₃) 6.83 (1H, m, ArH), 6.73 (1H, dd, J ArH = 7.9 Hz, J ArH = 7.8 Hz), 6.67 (2H, m, ArH), 3.31 (3H, bs, NH), 3.11 (2H, t, CH₂, J = 7.1 Hz), 1.67 (2H, q, CH₂, J = 7.1 Hz), 1.43 (2H, m, CH₂), 1.23–1.37 (28H, m, CH₂), 0.88 (3H, t, CH₂, J = 7.0 Hz); δC (100 MHz, CDCl₃) 137.39, 134.11, 130.72, 118.87, 115.67, 112.48, 53.39, 29.59, 29.71, 29.68, 29.64, 29.53, 29.50, 29.38, 27.39, 27.27, 21.13; m/z (EI) 360 (3%), 350 (1%), 349 (3%), requires M⁺ 360.3504.

Octadecyl-1,2-diaminobenzene d2 4k: Compound 4k was prepared according to the procedure described for compound 4a (91%), mp 53–54 °C (vapour: DRIFT [cm⁻¹] 3377, 3296, 2920, 2854, 2515, 2087, 1650, 1521, 1469, 1453, 1317, 1274, 1125, 1095, 741, and 722; δH (500 MHz, CDCl₃) 6.83 (1H, m, ArH), 6.73 (1H, dd, J = 7.9 Hz, J = 7.8 Hz), 6.67 (2H, m, ArH), 3.31 (3H, bs, NH), 1.65 (2H, m, CH₂), 1.42 (2H, m, CH₂), 1.23–1.35 (28H, m, CH₂), 0.88 (3H, t, CH₂, J = 6.8 Hz); δC (500 MHz) 137.76, 133.99, 120.64, 118.39, 116.40, 111.76, 31.81, 29.59, 29.56, 29.52, 29.50, 29.39, 29.33, 29.25, 27.14, 22.58, 14.00; m/z (EI) 362 (Found: M⁺ 362.5380. C₈₂H₇₈N₂ requires M⁺ 362.3628).

β-(1,2-Octadecylamino)-2-benzylbenzene 5a: 1-Octadecyl-1,2-diaminobenzene d2 4k: Compound 4k was prepared according to the procedures described for compound 4a (91%): mp 90–93 °C (vapour: DRIFT [cm⁻¹] 3403, 3346, 2919, 2489, 1620, 1546, 1519, 1471, 1403, 1323, 1285, 1219, 1067, 835, 742, 717, and 555; δH (400 MHz, CDCl₃) 9.33 (1H, s, ArH), 9.21 (2H, m, NH), 7.10 (2H, m, ArH), 6.94 (2H, d, ArH, J = 7.8 Hz), 6.57 (4H, m, ArH), 5.72 (1H, s, ArH), 5.26 (4H, t, CH₂, J = 7.1 Hz), 1.49 (4H, d, CH₂, J = 6.6 Hz), 1.31–1.36 (60H, m, CH₂), 0.84 (6H, t, CH₂, J = 6.9 Hz); δC (500 MHz) 147.53, 126.89, 126.85, 125.93, 46.93, 43.88, 31.72, 29.48, 29.44, 29.38, 29.17, 29.12, 26.93, 22.43, 13.76; m/z (FAB) 885 (Found: M⁺ 885.6954. C₃₀H₂₂₂N₂O₂ requires M⁺ 885.6945).

β-(1,2-Octadecylaminophenoxy)-2,4-dinitrobenzene d5: Compound 5d was prepared according to the procedure described for compound 4a (92%): mp 95–96 °C (vapour: DRIFT [cm⁻¹] 3404, 3350, 2915, 2850, 2620, 1608, 1565, 1520, 1470, 1426, 1403, 1324, 1295, 1213, 1068, 835, 744, 717, and 554; δH (400 MHz, CDCl₃) 9.39 (1H, s, ArH), 9.21 (2H, m, NH), 7.11 (2H, m, ArH), 6.92 (2H, dd, ArH, J = 7.6 Hz, J = 1.3 Hz), 6.57 (4H, m, ArH), 5.72 (1H, s, ArH), 5.26 (4H, t, CH₂, J = 7.1 Hz), 1.49 (4H, d, CH₂, J = 6.6 Hz), 1.31–1.36 (60H, m, CH₂), 0.84 (6H, t, CH₂, J = 6.9 Hz); δC (500 MHz) at 323 K C₄₃H₃₀O₃Cl₇ 147.50, 126.89, 126.85, 125.93, 96.49, 36.19, 29.31, 29.29, 29.46, 29.30, 29.23, 26.92, 22.46, 13.81; m/z (EI) 889 (Found: M⁺ 888.7118. C₃₀H₂₂₂N₂O₂Cl₇ requires M⁺ 888.7118).