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Liquid Crystals

Spontaneous Deracemization of Disc-like Molecules in the Columnar Phase

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Spontaneous deracemization is among the more important topics in chemistry. Many examples of deracemization have been reported ever since Pasteur's famous experiment. Deracemization can occur when racemic molecules are crystallized, and even in liquid-crystalline phases. The discovery of polar switching[1] and layer chirality[2] in bent-core mesogens has stimulated the study of chirality in nonchiral molecular systems. The spontaneous formation of macroscopic chiral domains in bent-core mesogens has been reported by many research groups.[3] Inherent chirality in achiral bent-core mesogens has been attributed to an axially chiral molecular conformation as evidenced by polarized IR spectroscopy[4] and NMR spectroscopy.[5] Quantum chemical calculations have revealed that the most stable conformation of the molecular core is a propeller-like twist.[6] The close packing of such molecules to chiral superstructures results in macroscopic chiral domains.[7] A similar scenario was found to work even in rod-like molecules.[8] The situation is slightly different in columnar phases. Extensive studies have been conducted to investigate the formation of chiral columns or helical superstructures in chiral and nonchiral disc- or star-like molecules, as well as other molecules with more complicated shapes.[9] Although the formation of a helical phase was reported in a highly ordered columnar phase consisting of a nonchiral triphenylene derivatives,[10] it was later found that the phenomenon actually occurred in a crystalline phase.[11] Thus, spontaneous deracemization has never been unambiguously demonstrated in discotic columnar phases consisting of nonchiral or racemic molecules. Herein we report the spontaneous deracemization (chiral resolution) of disc-like molecules in the columnar phase. Molecules appear to be flat, but not quite; they are slightly twisted. With the use of electronic and vibrational circular dichroism (ECD and VCD) spectroscopy we found that such racemic disc-like molecules with axial chirality macroscopically segregate into chiral domains.

Liquid-crystalline molecules with a dibenzo[*g*,*p*]chrysene core were synthesized, and their mesogenic properties have been recently reported.[12] In one of the homologues with eight terminal -$OCOC_7H_{15}$ chains (Figure 1), we observed only one transition from the isotropic phase to a columnar phase at 229.6 °C (see DSC data in Figure S1 in the Supporting Information). Textures in the columnar phase, shown in Figure S2 in the Supporting Information, seem to be those of the conventional plastic columnar (Col_p) phase.[13] According to X-ray diffraction data, however, we observed no noticeable diffraction peaks in a wide-angle region, which is unlike a highly ordered Col_p phase (see Figure S3 in the Supporting Information). Apparently the compound used is not solid, but paste-like at room temperature, indicating a noncrystalline columnar phase.

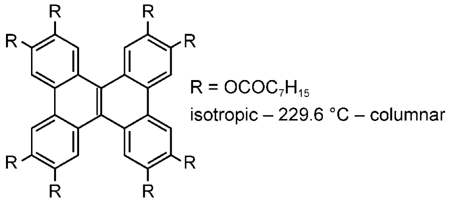

Figure 1. Structure and phase sequence of the disc-like molecule with a dibenzo[*g*,*p*]chrysene core.

To obtain some basic information on the aromatic core, we performed quantum chemical calculations using the Gaussian 03 software package[14] at the B3LYP/6-31G (d,p) level. First we calculated the stable structure of the dibenzo[*g*,*p*]chrysene core terminated with hydrogen atoms. The stable structure is twisted because of the steric repulsion between hydrogen atoms, as reported previously.[15] The top and side views of the molecule are shown in Figures 2a and b, respectively. The twisting angle between the wings is 35°. The side view of the twisted core is modeled below, with solid and broken lines representing the proximal and distal wings, respectively.

To estimate energy barriers, we calculated the energies of the stable chiral conformations and the transition state between the two. The result is depicted in Figure 2c. Relative energy levels were set with the most stable conformation considered as zero energy. One might initially imagine that the molecule adopts a flat conformation at a transition state between two stable states. This is reasonable from a symmetry standpoint, as the chiral exchange occurs with maintenance of D_2 symmetry. We found, however, that a flat conformation is not likely the transition state, as it has a very high energy

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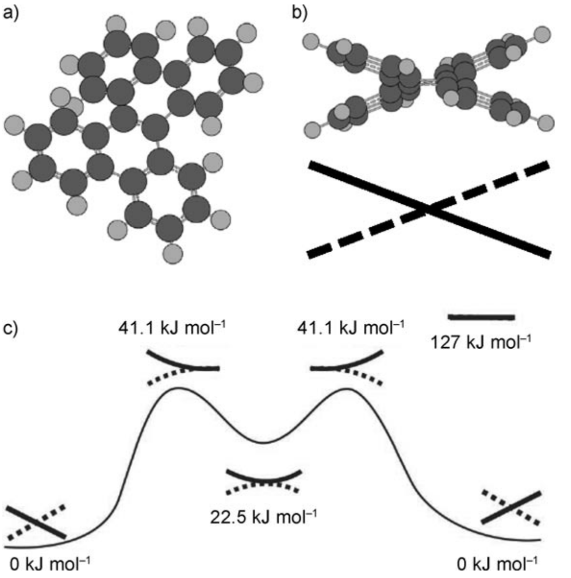

Figure 2. a) Top and b) side views of the stable conformation of the discotic core optimized by quantum chemical calculations at the B3LYP/6-31G (d,p) level. The two wings of the molecule in side view are represented by solid (proximal) and broken (distal) lines. c) Energy diagram for the transition between two chiral conformations. Energies were calculated at the B3LYP/6-31G (d,p) level with zero-point energy correction.

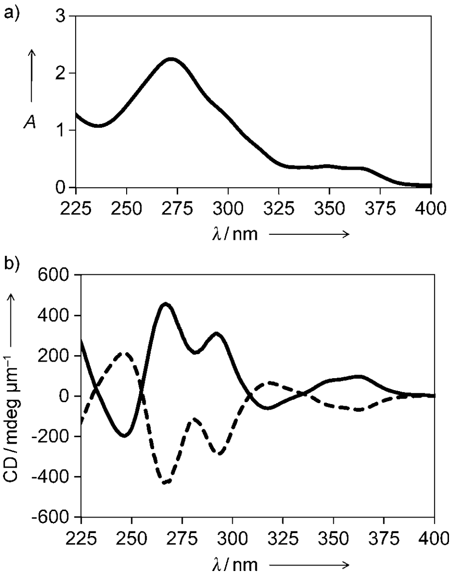

Figure 3. a) UV/Vis absorption and b) ECD spectra in the columnar phase at room temperature. Large ECD peaks were observed in an absorption region; mirror-image spectra were obtained from large chiral domains.

(127 kJ mol^{-1}). Instead, an achiral metastable state emerges at 22.5 kJ mol^{-1} via transition states at 41.1 kJ mol^{-1}. Hence the chiral exchange of this aromatic core occurs by two steps through an achiral metastable state. The energy barrier between chiral conformations (41.1 kJ mol^{-1}) is much greater than the thermal energy at room temperature. However, it is still too small to isolate the chiral conformation,[16] so that two chiral conformations exist equally at the molecular level. Therefore, this aromatic core is still macroscopically achiral.

For ECD measurements, we prepared thin cells with a thickness of approximately 500 nm, by which we were able to observe unsaturated reliable absorption and ECD spectra.[17] In contrast to the characteristic texture of a thicker cell (2.8 μm; Figure S2a in the Supporting Information), a simple and rather uniform texture emerged in the thin cell (Figure S2b in the Supporting Information). Figures 3a and b respectively show the absorption and ECD spectra in the columnar phase at room temperature. To confirm the lack of influence on ECD signals from birefringence, we measured the ECD spectra by rotating the cell about the cell surface normal. We observed only small changes in the spectra, as shown in Figure S4 in the Supporting Information. Absorption bands between 225 and 400 nm are attributed to the aromatic core. Two observations can be made with the ECD spectra: 1) ECD peaks appear in a wavelength range corresponding to the absorption peaks, and 2) the ECD spectra taken in different chiral domains are mirror images to each other. In fact, we obtained a single chiral domain almost exclusively with the use of thin cells. Therefore, CD measurements through a pinhole with a diameter of approximately 1 mm gave the same sign and nearly the same intensity from different positions of the sample. However, repeated experiments after heating to the isotropic phase gave positive and negative signals with equal probabilities, as shown in Figure 3b.

To confirm the origin of chirality discussed based on the quantum chemical calculation, we performed VCD measurements. Figure 4 shows the a) IR absorption and b) VCD spectra in the columnar phase at room temperature. The main VCD peaks emerge at IR absorption wavelengths as mirror images, as is the case with ECD. The main peaks observed are: 1) C=O stretching of an ester (1760 cm^{-1}), 2) C–C stretching of an aromatic ring (1500 cm^{-1}), and 3) C–O–C stretching of an ester (1260 and 1150 cm^{-1}). The VCD peak of

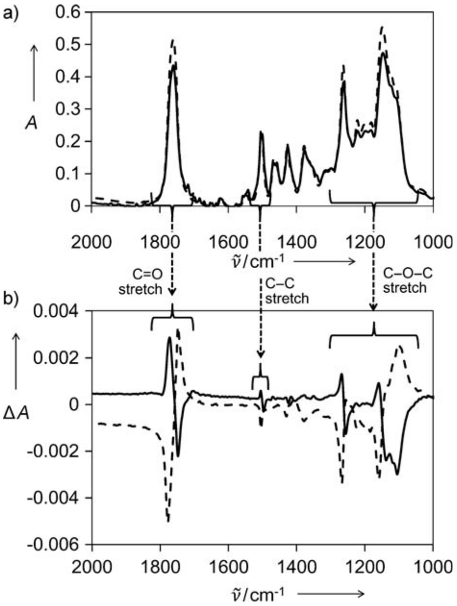

Figure 4. a) IR absorption and b) VCD spectra in the columnar phase at room temperature.

C–C stretching originates from the chiral conformation in the molecular core. If the dibenzo[*g*,*p*]chrysene core had a flat achiral conformation, no signals would appear around this absorption band. The chirality transfer occurs from the chiral molecular core to the achiral terminal alkyl chains. Hence, the VCD peaks of C=O and C–O–C stretching of an ester are associated with the twisted conformation in the core.

The presence of CD signals strongly indicates that the molecules segregate into macroscopic chiral domains. For such deracemization to occur, formation of chirality at two levels is necessary: 1) only molecules with the same chirality stack in one column, and 2) only columns with the same chirality segregate into macroscopic chiral domains. Chiral column formation (1) is the result of close packing of chiral molecules with a twisted conformation. However, chiral domain formation (2) cannot be readily understood by packing effects, owing to the surrounding alkyl chains. We found that molecules with -OCOC$_{15}$H$_{31}$ terminal alkyl chains show the Col$_h$ phase and do not exhibit the deracemization phenomenon. In contrast, the present molecules with shorter -OCOC$_7$H$_{15}$ alkyl chains show an unknown columnar phase and undergo deracemization. Thus, chiral interactions between central column cores are not blocked by shorter terminal alkyl chains, and chiral superstructures can therefore form. Packing effects stabilize a twisted structure between neighboring columns; very high CD signal intensity ($>$400 mdeg μm^{-1}) is consistent with such chiral superstructures. A more detailed investigation of chiral superstructures will be part of our future work.

In summary, quantum chemical calculations along with ECD and VCD measurements were performed on a disc-like molecule with a dibenzo[*g*,*p*]chrysene core. This molecule appears to be nonchiral, but is indeed chiral according to quantum chemical calculations; that is, the most stable conformation of the molecular core has a propeller-like twist. The vibrational CD spectra reveal a twisted structure for the central core associated with ester linkages to alkyl chains. The close packing of twisted cores having the same chirality results in the formation of chiral columns. High-magnitude electronic CD signals reveal the formation of chiral superstructures such as aggregated structures of chiral columns with the same handedness and superhelical structures of chiral columns.

Experimental Section

We used fused quartz plates as the substrates with which to measure UV/Vis absorption and electronic circular dichroism (ECD) and fabricated sandwich cells. The cell thickness was ca. 500 nm. The detailed conditions for fabricating cells and performing measurements is described in reference [12]. We used SrF$_2$ substrates with 2 μm-thick polymer film spacers for vibrational circular dichroism (VCD) measurements. Both substrates were cleaned by a conventional process and were used without further surface treatment. UV/Vis, ECD, and VCD spectra were recorded with JASCO V-560, JASCO J-720WI, and JASCO FVS-4000 spectrometers, respectively.

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