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Structure and Morphology of Helicene Fibers

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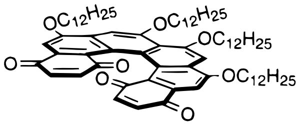
Abstract: Nonracemic helicene **1** when cooled from the melt organizes itself into macroscopic liquid crystalline fibers. Transmission electron microscopic analysis shows that the fibers are comprised of lamellae 50−200 nm wide, each only ca. 10 nm high. Analyses by X-ray and electron diffraction demonstrate that the molecules are organized in hexagonally packed columns. Polarized light microscopy reveals that the columns are stacked so that their long axes parallel the long axes of the fibers. In ultrathin films, the alkyl side chains organize themselves further as in crystalline alkanes.

Introduction

The material consisting of molecules of nonracemic helicene **1** exhibits two extraordinary properties, both attributable to molecular self-aggregation.[1] The first is an enormous ability to rotate the plane of polarization of plane-polarized light, much greater than that of dilute solutions of the comprising molecules. At the sodium D-line, the specific rotation is 1400 deg/mm, corresponding to $[\alpha]_D$ 170 000°, 280 times that of a dilute solution in *n*-dodecane. The second property is spontaneous organization of the molecules into macroscopic fibrous structures that are clearly visible under an optical microscope. While *solutions* of other molecules, notably amphiphiles[2] and gelators,[3] give rise to fibers, we have been unable to find another example of a pure material that in the absence of external forces[4] forms discrete isolated fibers from an isotropic melt.



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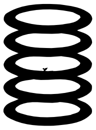

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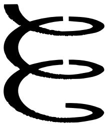

3

That molecules of **1** might aggregate seems plausible, for they appear to be helical analogues of molecules composed of planar aromatic cores surrounded by alkyl chains that organize into columnar liquid crystalline phases.[5] Whereas a columnar phase of the latter might be pictured as **2**, an analogue of helical molecules might be pictured as **3**.

That molecules of **1** do aggregate is evident from the properties of their solutions. In *n*-dodecane, when the concentration is increased to ca. 0.001 M, the CD and UV−vis spectra both shift,[6] the circular dichroisms and specific rotations become greatly enhanced, and there is an increase in light scattered at an absorption frequency.[1,7] Both the direction in which concentration shifts the absorption spectra and the absence of exciton splitting in the CD spectra imply that, as in **3**, the aggregated molecular helixes share a common axis.[1] In the pure material, it seems plausible that the molecules are similarly arranged, but if they are, it is unclear how such aggregates are organized within the fibers, which are very large, commonly ca. 250 nm wide—corresponding to ca. 60 molecular widths—and immeasurably long.

The experiments described below were carried out to answer this question. They analyze the molecular organization within the fibers by X-ray diffraction, electron diffraction, transmission electron microscopy (TEM), and polarized light microscopy, and they lead to the conclusions that the molecules do in fact stack in columns, much as in structure **3**, and that the fibers are comprised of lamellar arrays of the helical columns arranged as indicated in Figure 1.

Experimental Section

The methods by which the samples were prepared are described at appropriate places in the following section. The instrument used for the electron diffraction and TEM measurements was a JEOL transmission electron microscope operating at 100 keV and equipped with a rotation-tilt stage. Diffraction patterns of Ni-filtered Cu Kα X-rays at 40 kV and 25 mA were recorded in the reflection geometry. The

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† Bell Laboratories.

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[1] Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767.

[2] Fuhrhop, J.-H.; Helfrich, W. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 1565.

[3] Example of aromatic molecules that gel organic solvents: (a) Lin, Y.; Kachar, B.; Weiss, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 5542. (b) Snijder, C. S.; de Jong, J. C.; van Bolhuis, F.; Feringa, B. L. *Chem. Eur. J.* **1995**, *1*, 594. (c) van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Tetrahedron Lett.* **1997**, *38*, 281. (d) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957. (e) Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J.-P. *J. Chem. Soc., Chem. Commun.* **1991**, 416.

[4] Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1 (Crystal Structure, Morphology, Defects), Chapter 3, Section 3.8.

[5] (a) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57 and references therein. (b) Destrade, C.; Foucher, P.; Gasparoux, H.; Tinh, N. H.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (c) *Metallomesogens*; Serrano, J. L., Ed.; VCH: New York, 1996. (d) Simon, J.; Bassoul, P. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 2, Chapter 6. (e) Serrette, A. G.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 2252.

[6] Also the fluorescence emission spectrum of **1** shifts when its concentration in *n*-dodecane is raised from 0.021 mM to 21 mM.[1]

[7] Unpublished experiments by Colin Nuckolls show that the shifts and enhancements extend to solutions as dilute as 0.001 M.

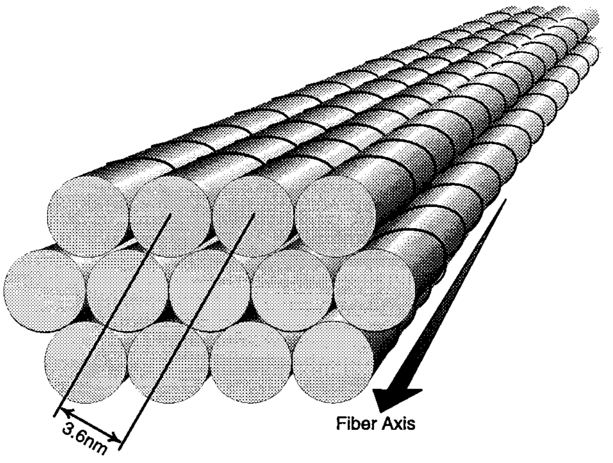

Figure 1. Schematic representation showing how columns of helicenes **1** are organized in the fibers. The hexagonal lattice parameter *a* is 4.14 nm.

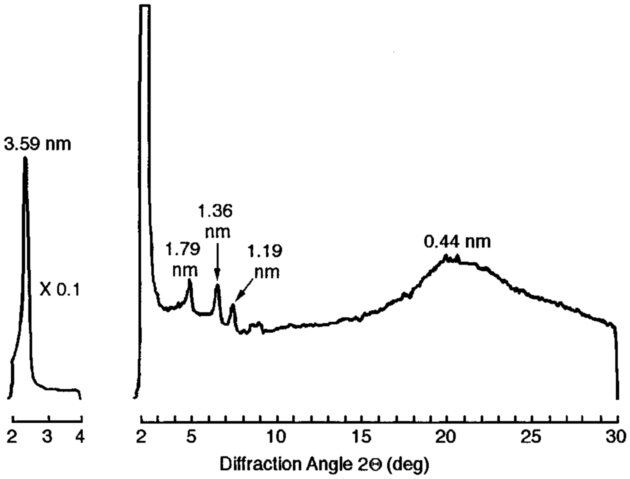

Figure 2. Diffraction pattern of X-rays reflected from a glass surface coated with fibers of **1**.

polarized light microscope had a rotating stage and accepted auxiliary compensators.

Results and Discussion

X-ray Diffraction. A fibrous sample for analysis was prepared by heating levorotatory **1**[1] on a glass plate until the material became an isotropic liquid (211 °C) and then cooling it at a rate of 10 °C/min. The diffraction pattern shown in Figure 2, of X-rays reflected from the surface, is overwhelmingly dominated by a peak at 3.59 nm, similar to diffraction peaks displayed by columnar discotic liquid crystals and identified with their intercolumnar spacings.[5,8] Another similarity of the diffractograms of **1**'s fibers and those of columnar discotic liquid crystals[8] is the paucity of other peaks. The implication is that the molecules in the fibers of **1**, like those in discotic mesophases, are ordered in columns as one-dimensional liquids.[5a]

Other features that *are* observed in the diffractogram of **1**'s fibers (Figure 2) are a set of weak sharp peaks that include (at 1.79 nm and at 1.19 nm) the second and third-order reflections from the crystal planes separated by 3.59 nm and a peak at 1.36 nm, which, because it equals $1/(7^{1/2})$ of 3.59 nm, implies that columns of helicenes are packed on a hexagonal lattice as in Figure 1.[9] In addition, there is a very broad peak centered at ca. 0.44 nm, also a characteristic of columnar discotic liquid crystals and assigned to the distance between their packed side-chains.[5d−e,8,10] This last peak could also include interplanar reflections between the core rings.[11] (In ordered columnar structures the mean tail−tail and core−core distances are the same.[8h]) However, a sharp peak for the spacing between planes containing the core rings, usually observed in the diffraction patterns of columnar discotic liquid crystals,[5d−e,8a−g,i,10] is not seen, possibly because adjacent molecules may fluctuate from exact parallelism.

An alternative preparation of material for X-ray diffraction analysis, a 0.5 mm wide collection of thin fibers, each 20−50 μm in diameter, that were pulled from evaporating 3 mM benzene or hexane solutions on a water surface, yielded X-ray diffraction patterns essentially identical with those provided by the fibers described before, which were formed thermally.[12]

Transmission Electron Microscopy/Electron Diffraction. The morphology of the fibers was examined by TEM, and the organization of the molecules within the fibers was analyzed by electron diffraction. To minimize destruction of crystallinity by the electron beam, the sample was scanned in the diffraction mode under low-dose conditions. When a suitable region was found, its diffraction pattern was immediately photographed, and only subsequently was the morphology of that same region recorded by bright-field TEM.

Samples were prepared by casting thin films of **1** from a dilute heptane solution onto a freshly exposed mica surface, heating them (as described above) to 211 °C, and then cooling them to room temperature at a rate of 10 °C/min. The samples were obliquely shadowed with Pt evaporated at an angle of $\tan^{-1}$ 0.5 and coated with a patina of amorphous carbon to support them so they could resist distorting significantly under the impact of the electron beam.[13] Finally they were floated off in water onto the Cu grids used as the TEM supports and dried. The bright-field transmission electron micrographs then showed, as illustrated in Figure 3, that the fibers, which under the optical microscope appear cylindrical, are in fact composed of stacked ultrathin lamellae, ca. 10 nm high and 50−200 nm wide. If the preparative steps that involve heating to 211 °C and slowly cooling are bypassed, the lamellar morphology is much less distinct.

Individual fibers such as those of Figure 3 are too narrow to yield diffraction patterns that can be recorded before electron irradiation destroys their crystallinity. However, sharp diffrac-

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(8) (a) Levelut, A. M.; Hardouin, F.; Gasparoux, H.; Destrade, C.; Tinh, H. H. *J. Phys. (Paris)* **1981**, *42,* 147. (b) Levelut, A. M. *J. Phys. (Paris)* **1979**, *40,* L-81. (c) Mohr, B.; Wegner, G.; Ohta, K. *J. Chem. Soc., Chem. Commun*. **1995**, 995. (d) Kumar, S.; Wachtel, E. J.; Keinan, E. *J. Org. Chem.* **1993**, *58,* 3821. (e) Simon, J.; André, J.-J.; Skoulios, A. *New J. Chem.* **1986**, *10,* 295. (f) Foucher, P.; Destrade, C.; Nguyen, H. T.; Malthete, J.; Levelut, A. M. *Mol. Cryst. Liq. Cryst.* **1984** *108,* 219. (g) Levelut, A. M. *J. Chim. Phys.* **1983**, *80,* 149. (h) Fontes, E.; Heiney, P. A.; Ohba, M.; Haseltine, J. N.; Smith, A. B., III *Phys. Rev. A* **1988**, *37,* 1329. (i) Sauer, T. *Macromolecules* **1993**, *26,* 2057.

(9) The 1.36-nm peak would then be the (210) reflection from the hexagonal lattice of Figure 1.

(10) Heiney, P. A.; Fontes, E.; de Jeu, W. H.; Riera, A.; Carroll, P.; Smith, A. B., III *J. Phys. France* **1989**, *50,* 461.

(11) In discotic liquid crystals the distances are between 0.33 and 0.56 nm (refs 5d, 5e, 8a−g, 8i, and 10). In crystals the distances are 0.34 nm for benzoperylene [(a) Cotrait, M. *C. R. Hebd. Sean. Acad. Sci. Paris, Ser. C* **1977**, *298,* 547], 0.34 nm for coronene [(b) Coucet, J.; Levelut, A. M.; Lambert, M. *Acta Crystallogr.* **1979**, *B35,* 1102], and 0.35 nm for naphthoquinone [(c) Gaulter, P. J.; Christian, H. *Acta Crystallogr.* **1965**, *18,* 179].

(12) The X-ray diffraction was recorded in a vacuum with use of Ni-filtered Cu $K\alpha$ radiation. The intense peak and the second- and third-order peaks for the 3.6-nm spacing, as well as broad diffuse outer rings in the region 0.3−0.5 nm, were seen. There was no orientational preference, indicating that fibers prepared in this way are organized in the same way as those prepared by heating and cooling, but are comprised of random aggregates.

(13) Grubb, D. T. *J. Mater. Sci.* **1974**, *9,* 1715.

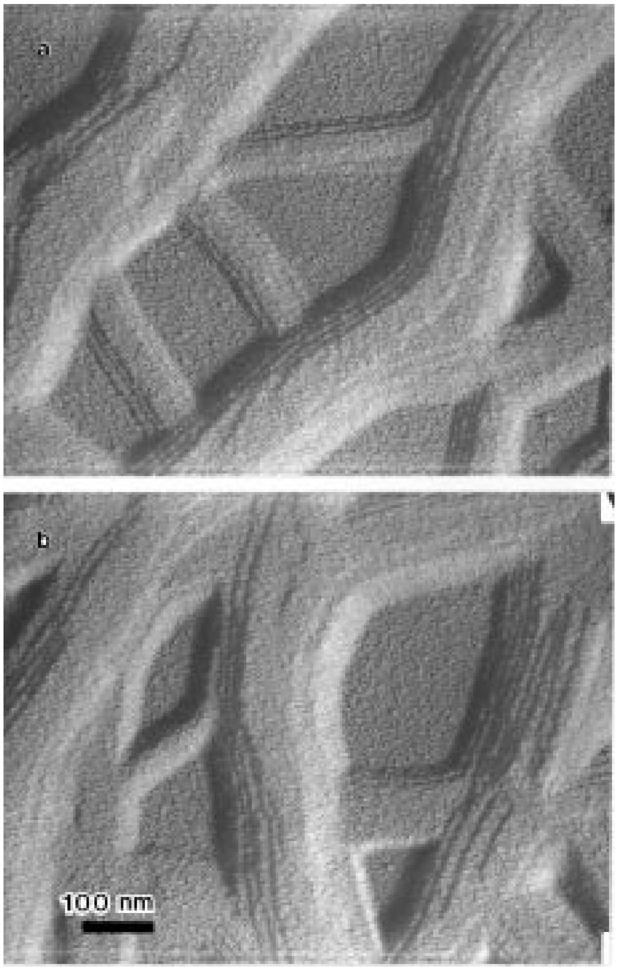

Figure 3. Transmission electron micrograph of fibers of **1**, illustrating (a) the continuity of individual lamellae over μm distances and (b) that the stacks can reach a height of at least eleven lamellae.

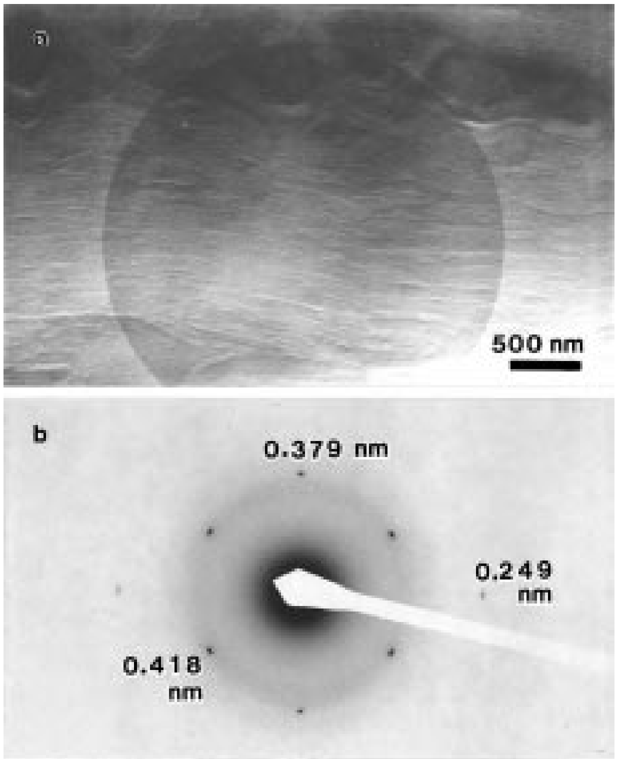

Figure 4. (a) Transmission electron micrograph of a region in which individual multilamellar fibers have aggregated to a width of over 1.5 μm and (b) the electron diffraction pattern from the circular region in part a. The pattern is rotated to be correctly oriented with respect to the field of view. The circular area in part a is a double exposure of the diffraction aperture.

tion could be recorded from areas in which fibers are aggregated into broad assemblies (≥ 1 μm wide) with a common orientation (see Figure 4). The patterns reveal a rectangular lattice with spacings of 0.249, 0.379, and 0.418 nm (Figure 4). These spacings and orientations correspond closely to those of the (020), (200), and (110) reflections of polyethylene,[14] suggesting that in these regions the dodecyl side chains adopt extended conformations and are packed in the same way as the hydrocarbon chains of polyethylene[14] and normal alkanes.[15] Because all the observed reflections belong to the *hk*0 net, the chains that give rise to them must be nearly perpendicular to their constituent lamellae.

But the long axes of the helicene columns cannot also be perpendicular to the lamellae, because the exceptionally strong reflection at 3.59 nm seen in the X-ray diffraction (Figure 2) is absent in the electron diffraction from thin samples. This diffraction peak does, however, attain the reflecting position if the sample is tilted about the axis of the fibers by 30° in either direction.[16,17] Then the intense reflections shown in Figure 5 appear, transverse to the tilt axis and corresponding to a measured spacing of 3.51 nm. In thicker regions of the sample, where the fibers consist of lamellae that are skewed from the surface at a variety of angles, the 3.51-nm reflections are observed even when the sample is not tilted and, significantly, they are transverse to the fiber axes (see Figure 6).

There are two ways in which columns of molecules may be organized in the fibers that would account for the diffraction patterns observed. The first is illustrated schematically in Figure 1 and the second in Figure 7. In either case, a tilt of 30° about the fiber axis would move crystallographic planes separated by 3.5−3.6 nm to parallelism with the electron beam and therefore to the reflecting position, where they would give rise to diffraction spots transverse to the fiber axis.

Consider first the arrangement in Figure 1. The geometry of the hexagonal lattice requires that the diameter of the helicene columns be 4.1 nm, which is close to the 4.4 nm estimated as the diameter of a column of molecules **1**: the sum of the diameter of the aromatic core (0.96 nm, estimated with the aid of the MacroModel computer program[18]) plus the length of two fully extended dodecyl chains (ca. 3.46 nm[19]). That the calculated diameter of the helicene columns slightly exceeds the intercolumnar distance agrees with similar observations made for discotic liquid crystals, whose side chains are proposed to interdigitate.[20] The measured height of individual lamellae (ca. 10 nm according to Figure 3) implies that they are only ca.

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[14] In polyethylene 0.249, 0.374, and 0.414 nm, respectively: Dorset, D. *Macromolecules* **1991**, *24*, 1175.

[15] Bunn, C. W. *Trans. Faraday Soc.* **1939**, 482.

[16] Spots separated by 60°, perpendicular to fibers and at low angles, expected for hexagonal order, have been observed in liquid crystalline fibers of triphenylenes [Chiang, L. Y.; Safinya, C. R.; Clark, N. A.; Liang, K. S.; Bloch, A. N. *J. Chem. Soc., Chem. Commun.* **1985**, 695] and truxenes (ref 8h).

[17] At angles greater than 30°, this reflection splits into two that are off-meridional and that move toward the tilt-axis as the tilt angle is increased.

[18] Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

[19] Each $2.54 \times 6 + 2.1 = 17.3$ Å, where 2.54 Å is the distance between every third atom (ref 15) and 2.1 Å is the van der Waals radius of a methyl (Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 261).

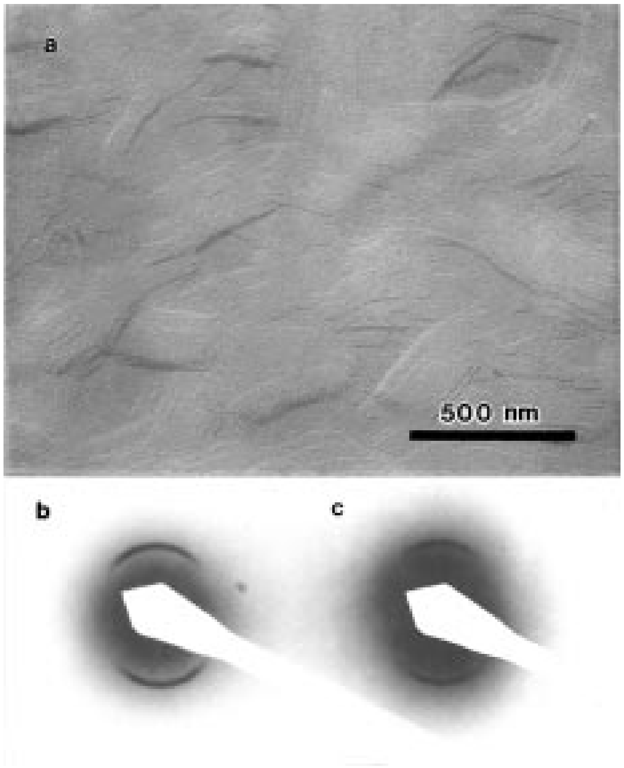

Figure 5. (a) Transmission electron micrograph of thin areas of **1**. Parts b and c show the strong meridional TEM reflections observed when the sample is tilted about the axis of the specimen holder (horizontal in the figure) either (b) 30° in one direction or (c) 30° in the other.

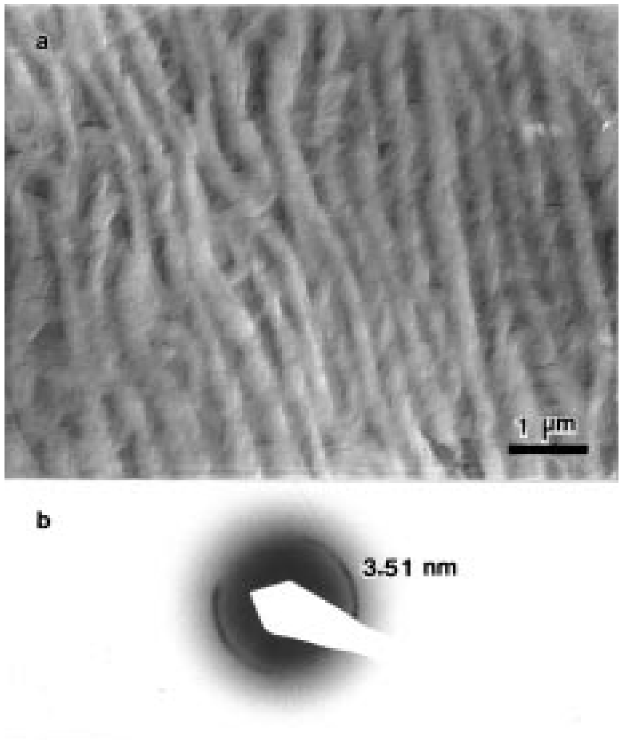

Figure 6. (a) Transmission electron micrograph from thick fibers of **1** and (b) its corresponding diffraction pattern (in correct mutual orientation). The electron beam is perpendicular to the plane of the specimen.

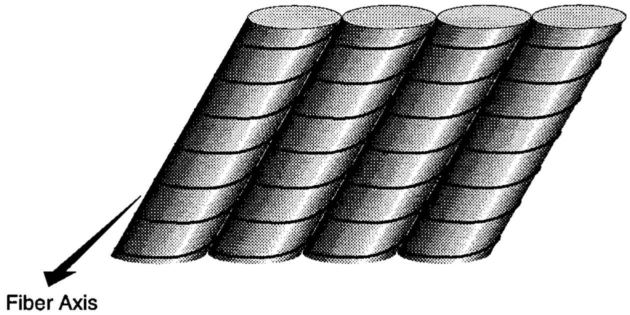

Figure 7. Schematic representation showing columns of helicenes **1** perpendicular to the fiber axis and tilted by 30° from the lamellar normal.

2−3 helicene columns high. That the side chains of the helicene are extended and in the mean aromatic plane accords with the conformation deduced by infrared analyses for liquid crystalline triphenylenes.[21] Some of these side chains could easily be perpendicular to the sample's surface, which would account for why the *hk*0 hydrocarbon electron diffraction spots are observed (Figure 4) when the samples are untilted. A feature that might have been expected of the structure, but that was not observed, is a diffraction spot at 2.1 nm, corresponding in Figure 1 to vertical planes separated by column radii (3.59/($3^{1/2}$) nm). In the diffractograms of columnar discotic liquid crystals, this peak is also either very weak[5e,8i,22] or unseen.

Instead of being organized as in Figure 1, the molecules might alternatively be organized in columns that, as in the illustration in Figure 7, have their long axes not collinear with the fiber axis, but inclined by 30° to it. It is an experiment using polarized light microscopy that identifies how the molecules are oriented with respect to the fibers and thus distinguishes the arrangements of Figures 1 and 7.

Polarized Light Microscopy. Figure 8a shows a set of macroscopic fibers under a microscope without polarizers, while Figure 8b shows the same view between crossed polars. That fibers, marked on the figure, are extinguished when parallel to the polarizer or analyzer (Figure 8b) and clearly visible when 45° to the crossed polars (Figure 8c) means that a vibration direction of the birefringent material is *uniformly* parallel to the fiber axis. The question is whether, if the fibers are uniaxial, this direction is that of the larger or the smaller refractive index. The answer is provided by views of the fibers when they are parallel and perpendicular to the slow vibration ray (or higher refractive index) of a unit retardation- (or first-order red-) plate interposed at 45° to the polars.[23] In fibers with the former orientation, the retardation is reduced to first-order yellow; in those with the latter, it is increased to second-order blue. The fibers therefore are negatively birefringent: the refractive index is lower along their length than perpendicular to it.[24] Since for aromatic molecules in general[25] and for columnar discotic liquid

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[20] In phthalocyanines: (a) Engel, M. K.; Bassoul, P.; Bosio, L.; Lehmann, H.; Hanack, M.; Simon, J. *Liq. Cryst.* **1993**, *15,* 709. (b) van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6,* 577. In triphenylenes: (c) Fontes, E.; Heiney, P. A.; de Jeu, W. H. *Phys. Rev. Lett.* **1988**, *61,* 1202. In truxenes: (d) Lejay, J.; Pesquer, M. *Mol. Cryst. Liq. Cryst.* **1984**, *111,* 293. In macrocyclic polyamides: (e) Lehn, J.-M.; Malthête, J.; Levelut, A.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1794.

[21] Yang, X.; Nitzsche, S. A.; Hsiu, S. L.; Collard, D.; Thakur, R.; Lillya, C. P.; Stidham, H. D. *Macromolecules* **1989**, *22,* 2611.

[22] Fischer, H.; Ghosh, S. S.; Heiney, P. A.; Maliszewskyj, N. C.; Plesnivy, T.; Ringsdorf, H.; Seitz, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 795.

[23] A similar technique was used to analyze the orientation of DNA molecules in a lyotropic liquid crystalline phase (Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P. *Nature* **1989**, *339,* 724).

[24] Hartshorne, N. H.; Stuart, A. *Crystals and the Polarising Microscope*, 3rd ed.; Edward Arnold Ltd.: London, 1960; p 290ff.

[25] Sundararajan, K. S. *Z. Kristallogr.* **1936**, *93,* 238.

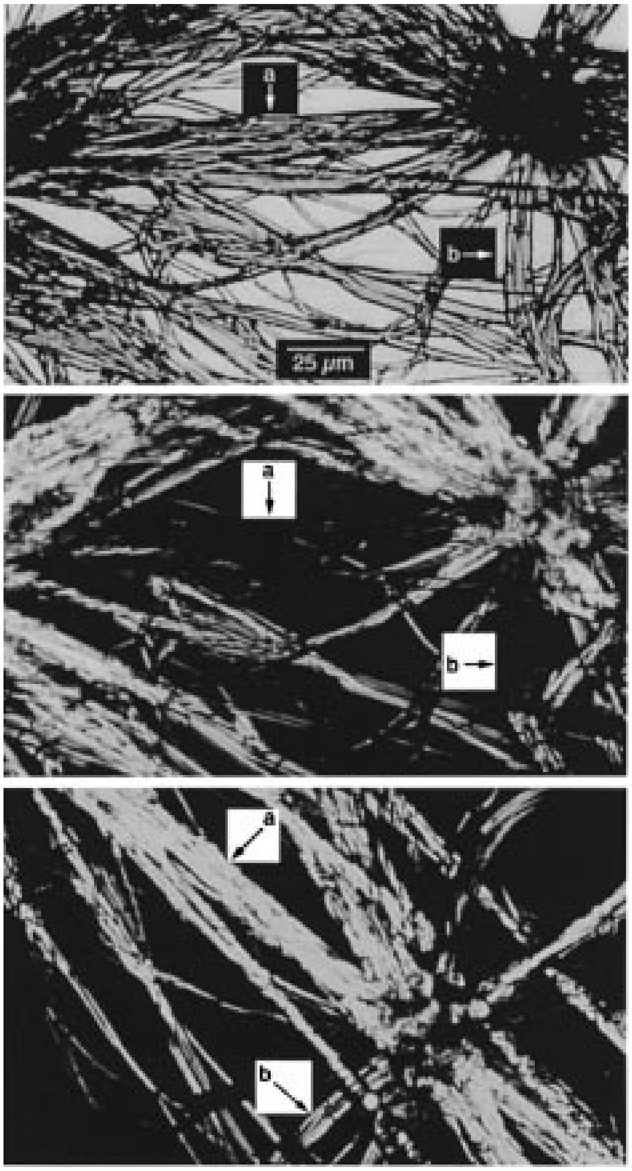

Figure 8. Optical microscopic views of a single set of fibers of **1** (a) between no polarizers; (b) between crossed polarizers, whose directions are horizontal and vertical in this figure; and (c) between crossed polarizers, but rotated by 45° from their position in part b. These show the extinction of fibers at positions marked **a** and **b**.

crystals in particular,[26] the refractive index is lower perpendicular to the molecular plane than in it, the experiment shows that the helix axes of **1** are oriented parallel to the fibers. Since the helixes are organized in columns, these columns run along the fiber axis as in Figure 1.

It is unclear how this organization relates to published knowledge. Like the fibers formed by pulling strands from discotic mesophases of triphenylenes[16a] and truxenes,[8h] those formed by **1** have columnar axes aligned parallel to the axes of the fibers. However, columnar discotic liquid crystals sometimes stack parallel[5e,27] and sometimes perpendicular[26,28] to the surfaces on which they lie.

Models were studied for insight into the molecules' stacking behavior. It appears that a repulsive steric interaction between the carbonyls from two molecules of **1** related by a translation along the helix axis could be relieved by a rotation about the helix axis and a lateral displacement. The resulting molecular alignment has the virtue that it places an electron-deficient quinone of one molecule contiguous to an electron-rich phenyl ether of another.[29] More significantly, it accords with calculations carried out with the MacroModel[18] molecular mechanics program. A Monte Carlo search of the conformations of three helicenes (methyls were substituted for the dodecyl side chains) constrained by the MM3* forcefield and the requirement that the molecules stay within 0.5 nm of each other showed an energy minimum when the molecules are almost parallel (there was a deviation of ca. 20°), and the translation from one molecule to the next requires a displacement of 0.39 nm along the helix axis, a rotation of 90° around that axis, and a displacement of 0.21 nm perpendicular to it. This translation and rotation impose a periodic "wobble" on the columns.

It is interesting to note that the racemic analogue of **1** does not form fibrous structures.[30] The reason may be that even if the racemate could give segregated left- and right-handed stacks, they might not organize themselves into larger fibers because the helical or superhelical structures of adjacent columns could not register.[31]

Conclusions

The helicenes are stacked in columns with parallel helix axes. Long columns of helicenes running along the fiber's length and stacked as in Figure 1, two to three high and ca. 60 across, comprise lamellae. Stacks of the lamellae constitute fibers, which can be clearly resolved under the optical microscope.

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(26) Vauchier, C.; Zann, A.; LeBarny, P.; Dubois, J. C.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1981,** *66*, 103.

(27) Takabatake, M.; Iwayanagi, S. *Jpn. J. Appl. Phys.* **1982**, *21*, L685.

(28) (a) Kardan, M.; Kaito, A.; Shu, S. L.; Takur, R.; Lillya, C. P. *J. Phys. Chem.* **1987**, *91*, 1809. (b) Yang, X.; Nitzsche, S. A.; Hsu, S. L.; Collard, D.; Thakur, R.; Lillya, C. P.; Stidham, H. D. *Macromolecules* **1989**, *22*, 2611. (c) Perova, T. S.; Vij, J. K. *Adv. Mater.* **1995**, *7*, 919.

(29) Substituted naphthoquinones stack with the quinone of one molecule over the phenyl of its nearest partner: Gaulter, P. J.; Christian, H. *Acta Crystallogr.* **1965**, *18*, 179.

(30) Nuckolls, C.; Katz, T. J. Unpublished results.

(31) All nearest neighbors in a hexagonal array cannot have opposite handedness. See ref 4, p 87.