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Aggregation of Conjugated Helical Molecules

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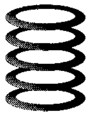
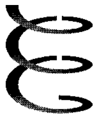
Suppose that appropriately substituted helical aromatic molecules, like their planar analogues (**1**),[1] organized spontaneously in the liquid phase into columnar aggregates (**2**). The structures would be novel. Moreover, if the structures promoted electronic interaction between constituent molecules, the optical and possibly other properties of the materials might be novel as well. To test this idea, **7** and **8** in Scheme 1 were synthesized optically active, and some of their characteristics were analyzed. Structure **8** was chosen because its preparation could be modeled on an efficient synthesis of a related helicene[2] and because donor-acceptor interactions between the electron-rich inner rings of one molecule and the electron-poor outer rings of another might stabilize a columnar stack.[3] The experiments show that **8** does aggregate spontaneously and that the aggregates exhibit specific rotations that are gigantic.


1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Scheme 1 outlines the syntheses; the accompanying supporting information provides the details both of these steps and of the preparation of the starting bis-enolether, **3**, from dehydroacetic acid. Both enantiomers of **7** and **8** were prepared. Both diasteriomers of **5** were analyzed by ^{1}H NMR spectroscopy to be >98% diastereomerically pure.

Evidence that molecules of **8** aggregate includes the following. Solutions of **8**, like solutions of aggregating molecules that have nonchiral chromophores attached to chiral groups,[4] exhibit circular dichroisms that are significantly enhanced by concentration. Figure 1a shows this effect for *n*-dodecane solutions in which the concentrations of **8** are 2.1×10^{-2} M and 2.1×10^{-5} M. Also, for **8**, as for aggregating nonhelical molecules,[5] different UV absorption (Figure 1b) and fluorescence emission (Figure 1c) spectra are displayed by concentrated and dilute solutions.[6] In addition, a 2.1×10^{-2} M solution of **8** in *n*-dodecane, like a similarly concentrated aqueous solution of the aggregating pseudoisocyanine,[7] is highly viscous. Moreover, Professor Peter Collings at Swarthmore College found that, for light near the absorption maximum, enhanced scattering attributable only to aggregates occurs when the concentration exceeds 1.5×10^{-2} M.[8] Finally, Figure 2 shows a striking manifestation of aggregation, the formation of fibers.[9] The fibers, which are displayed sandwiched between crossed polarizers, grow quickly and spontaneously when samples of **8** are cooled from a temperature at which they had become isotropic and free flowing (ca. 208 °C).[11] They are ca. 3 μm in diameter.[12] How their properties depend on their orientation remains to be analyzed, but the solutions described above are isotropic (at least optically).[13]

Not all helicenes surrounded by alkyl groups display the properties of aggregation described for **8**. Hexaether diacetate **7**, for example, does not. At room temperature, its UV absorption, fluorescence emission, and CD spectra in *n*-dodecane are essentially the same whether the concentrations are 2.1×10^{-2} M or 2.1×10^{-5} M,[14] possibly because intermolecular donor−acceptor interactions are absent or because increased steric crowding at the terminal rings destabilizes its aggregates.

It is unclear what the structures of **8**'s aggregates are, but the direction in which concentration shifts **8**'s longest wavelength UV absorption maximum (to the red,[5b,d,e,j,15] from 325 to 342 nm) implies that the transition dipoles excited in the aggregates are aligned approximately head-to-tail,[16] not head-to-head as in aggregates whose formation shifts UV absorptions to the blue.[4c,d,5a,f-j] This is reasonable if the electric vector of the light absorbed at ca. 333 nm is polarized along the axis of a helix similar to **2**. The parallel alignment of the transition dipoles would also account for the absence of splitting[17−20] in

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(6) On concentration, the fluorescence emission maximum shifts from 415 to 472 nm.

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(8) Pasternack, R. F.; Collings, P. J. *Science* **1995**, *269*, 935. We thank Prof. Collings for the preliminary result, whose details will be published separately.

(9) Solutions of numerous amphiphiles and a few other molecules[10] form fibers comprised of solute and solvent, but we could find no reports of fibers, like those pictured, that form in the absence of solvents.

(10) Examples are in the following and in the references cited therein. (a) Fuhrhop, J.-H.; Helfrich, W. *Chem. Rev.* **1993**, *93*, 1565. (b) Menger, F. M.; Lee, S. S.; Tao, X. *Adv. Mater.* **1995**, *7*, 669. (c) Snijder, C. S.; de Jong, J. C.; Meetsma, A.; van Bolhuis, F.; Feringa, B. L. *Chem. Eur. J.* **1995**, *1*, 594. (d) Hanabusa, K.; Okui, K.; Karaki, K.; Koyama, T.; Shirai, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1371. (e) Lin, Y.; Kachar, B.; Weiss, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 5542. (f) Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J.-P. *J. Chem. Soc., Chem. Commun.* **1991**, 416. (g) Jelley, E. E. *Nature* **1937**, *139*, 631.

(11) No other phase transitions between 25 and 200 °C were found by polarization microscopy or between 0 and 210 °C by DSC (scanned for two cycles at 10 deg/min), the latter implying that if any occur, they involve either little change in enthalpy or are slow. We thank Prof. Timothy Swager for the experiment.

(12) Estimated by Dr. N. D. Willmore, Harvard University.

(13) The solutions when sandwiched between crossed polarizers transmit no light. Their specific rotation is unchanged by a 90° turn of the cell.

(14) The spectra are in the supporting information. The only notable difference is in the molar ellipticity of a CD peak at 253 nm, which changes from -5.0×10^{5} in the dilute solutions to -5.5×10^{4} in the concentrated one.

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(16) Kasha, M. *Radiation Res.* **1963**, *20*, 55 and references therein.

(17) Splitting is observed when, as in refs 4 (for amphotericin also see ref 18) and 19, the vectors are not parallel. It is not observed in *J*-aggregates (see refs 5b,d and 20).

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(19) (a) Chen, H.; Law, K.-Y.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 7257. (b) Balaban, F. S.; Holzwarth, A. R.; Schaffner, K. *J. Mol. Struct.* **1995**, *349*, 183.

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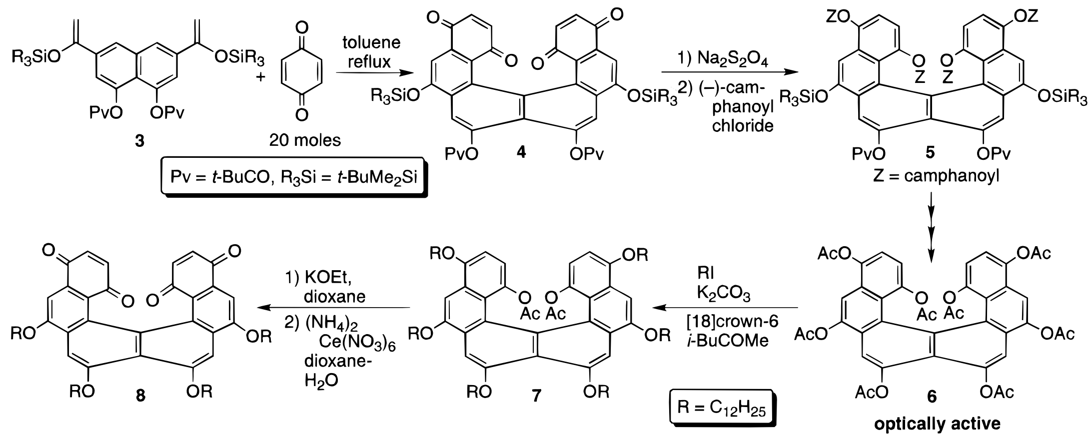
Scheme 1



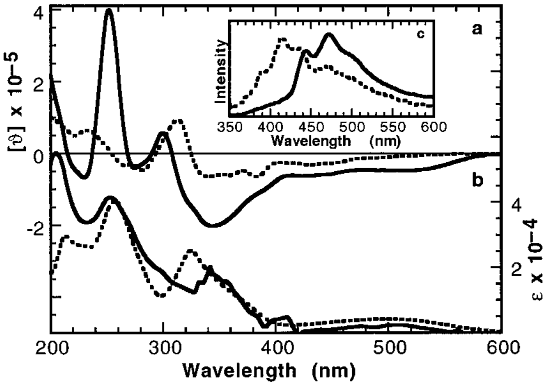


Figure 1. (a) CD spectra (ordinate on the left displaying molar ellipticities) and (b) UV absorption spectra (ordinate on the right displaying molar extinction coefficients) of **8** in *n*-dodecane: (—) when the concentration is 2.1×10^{-2} M and the path length 10 μm; (- - -) when the concentration is 2.1×10^{-5} M and the path length 10 mm. The inset (c) displays emission spectra (excitation at 325 nm) of these solutions. The path length was 10 μm.

the CD spectrum of the concentrated solution,[21] and the stacked structure would account for the aromatic and quinone ^{1}H NMRs shifting upfield by 0.09 ± 0.02 ppm when the concentrated solution is compared with the dilute.[22,23] The much greater breadth of the red-shifted absorption and emissions in **8** than in so-called *J*-aggregates[5b,e] might be expected if numerous stacks assembled into larger structures,[24] possibly ropes, and the spectrum varied with the location of the stack in the assembly.[25]

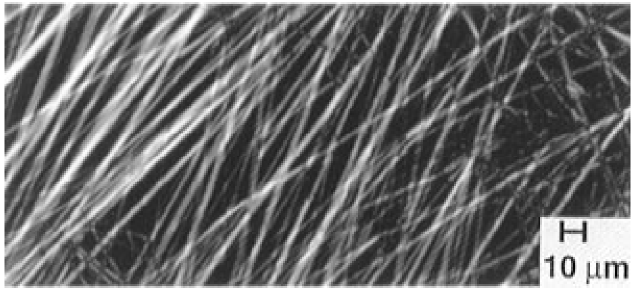


Figure 2. Optical micrograph of **8**, sandwiched between crossed polarizers, after it had been cooled to 195 °C from the isotropic liquid.

Whatever the nature of the aggregation, when it occurs, **8**'s specific rotation increases enormously. While concentrating *n*-dodecane solutions of **7** from 2.1×10^{-5} M to 2.1×10^{-2} M increases their $[\alpha]_D$ from 410 to 413 deg cm^2/g, similarly concentrating solutions of **8** increases their $[\alpha]_D$ from 678 to 8400 deg cm^2/g. More significantly, while neat samples of **7** (an isotropic lemon−yellow liquid) rotate plane-polarized light at the D-wavelength (589 nm) 11 deg/mm,[26] corresponding to an $[\alpha]_D$ of 1300 deg cm^2/g,[27] neat **8** (a red translucent wax) rotates it 1400 deg/mm,[26] corresponding to an $[\alpha]_D$ of 170 000 deg cm^2/g.[27,28] The figures for **8** are enormous and comparable only to the rotations plane-polarized light undergoes when traveling the helix axis of cholesteric liquid crystals.[29]

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Supporting Information Available: Experimental details of the syntheses of **7** and **8**. Spectra of new materials. UV, CD, and fluorescence spectra of **7** (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(22) The solvent was *n*-$C_{12}D_{26}$.

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(26) Measured using a 10 μm cell. The polarimeter measures an average over a ca. 7 mm^2 area.

(27) Calculated assuming the density to be 0.85 g/mL.

(28) The figures for **8** are reproducible and unchanged when samples are sheared in different directions. Prof. Collings found that at 633 nm, samples of **8** exhibit specific rotations as high as 2000 deg/mm. We thank him for the information.

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