Long Organic Fibers Obtained by Noncovalent Synthesis

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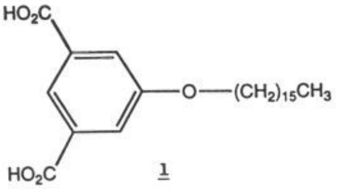
Chemists involved with "systems research" [1] delight in the rods, worms, tubules, ribbons, and laminates that noncovalent association affords them.[2] Whereas conventional synthetic chemistry constructs molecules *via* covalent bonds, "systems research" constructs molecular assemblies *via* noncovalent bonds. Recently, we examined a simple organic compound, **1**, designed in the hope



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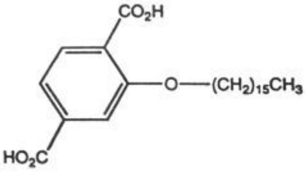
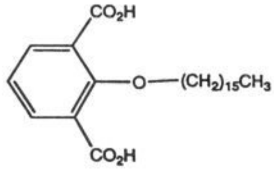
that it might aggregate in a "circular" fashion as a result of two cooperating noncovalent forces: hydrogen bonding among the *meta*-disposed carboxyls and hydrophobic association among the long hydrocarbon tails. Compound **1** was found to form flexible fibers up to several centimeters in length (Figure 1). We now relate our attempts to characterize this unique organic assembly.

Compound **1** becomes water-soluble above 78 °C in the presence of 2 equiv of KOH. Upon cooling, whiskers precipitate in a mass from solution. The material then can be removed by filtration, washed, and dried. Elemental analysis disclosed that the fibers are composed of the monopotassium salt of **1**. Thus, 2 equiv of KOH are required to dissolve **1** in water, but one of the resulting carboxylates must (despite the basic conditions) reprotonate itself during fiber formation. Although wet fibers are easily bent without obvious structural damage, dry fibers are extremely fragile. Hydration of the dry fibers restores their flexibility. Wet fibers are stable indefinitely (>1 year). Additional properties are listed below.

(a) Dry **1** (monopotassium salt) shows no phase transition from 5 °C to 100 °C as judged by differential scanning calorimetry; no melting occurs up to 200 °C.

(b) Fibers are not formed with the two isomers of **1** drawn below.





(c) Deleting one of the carboxyls in **1** prevents self-assembly into fibers.

Figure 1. A fiber composed of the monopotassium salt of 5-(hexadecyloxy)isophthalic acid.

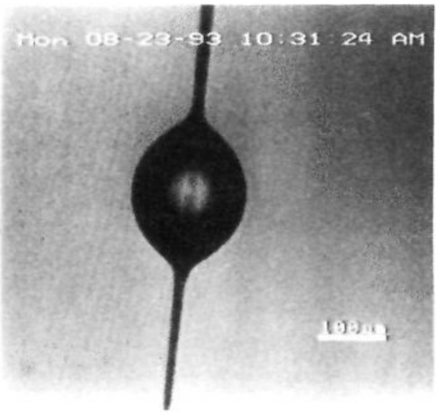
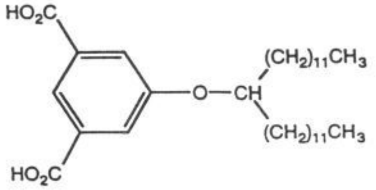


Figure 2. A water droplet on a fiber of **1** (phase-contrast light microscopy). Bar = 100 μm.

(d) Fibers fail to form when the chain is shortened from 16 carbons to 12 carbons. No fibers were observed with a tail consisting of $(CH_2)_3C{\equiv}CC{\equiv}C(CH_2)_{11}CH_3$.

(e) A double-tailed analog of **1**, drawn below, forms vesicles in basic water rather than precipitating out as fibers.



(f) Whiskers can be prepared with 2 equiv of NaOH, KOH, RbOH, and CsOH but not with LiOH and NH_4OH.

(g) The surface of the fibers is hydrophilic as indicated by the spreading of a water droplet (Figure 2).

(h) An attempt was made to observe fiber formation by light microscopy, but only small platelets appeared in the thin aqueous film as it cooled below 78 °C. Fibers are clearly in a delicate balance with other self-assembled states.

(i) Phase-contrast light microscopy of a damp fiber preparation showed an array of diameters, the thickest of which is about 3 μm (Figure 3). The entangled fibers can be manually "stretched" to form a filament several centimeters long. When such a filament is supported only at its termini, the suspended fiber sags at the middle but otherwise maintains its structural integrity even when dried.

(j) Scanning electron microscopy shows that a filament is in fact a bundle of small fibers (Figure 4). The thinnest whisker

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[1] Menger, F. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1086.

[2] Examples (representing six nations) can be found in the following references: Fuhrhop, J. H.; Wolfgang, H. *Chem. Rev.* **1993**, *93*, 1565. Nakashima, N.; Asakuma, S.; Kunitake, T. *J. Am. Chem. Soc.* **1985**, *107*, 509. Khatory, A.; Lequeux, F.; Kern, F.; Candau, S. J. *Langmuir* **1993**, *9*, 1456. Berret, J.-F.; Appell, J.; Porte, G. *Langmuir* **1993**, *9*, 2851. Archibald, D. D.; Mann, S. *Nature* **1993**, *364*, 430. Nusselder, J. J. H.; Engberts, J. B. F. N. *J. Org. Chem.* **1991**, *56*, 5522. Menger, F. M.; Lee, J. J.; Hagen, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 4017.

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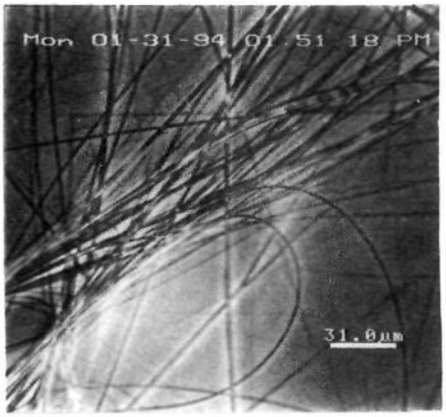

Figure 3. Phase-contrast photomicrograph of a damp fiber preparation. Bar = 31 μm.

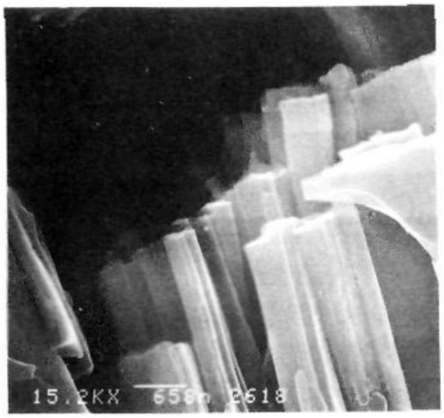

Figure 4. Scanning electron microscope image of a 5-nm Au/Pd-coated fiber. Bar = 658 nm.

that we have been able to detect is only about 27 nm in diameter, but it is unknown whether this represents the "unit fiber". When a filament is physically pulled apart, the center becomes thinner, showing that the component fibers can easily slide by one another. No evidence was obtained that fibers are hollow.

The model in Figure 5, in which **1** self-organizes into disks that then stack one upon one another, is consistent with all of our observations. The component disks are stabilized by a combination of hydrogen-bonding and hydrophobic forces. Stacking of the disks is favored by hydrophobic association at the disk interior and (possibly) interdisk chain entanglements. The model is vaguely reminiscent of discotic mesophases[3] except that the hydrophobic chains point inward instead of radiating outwardly.

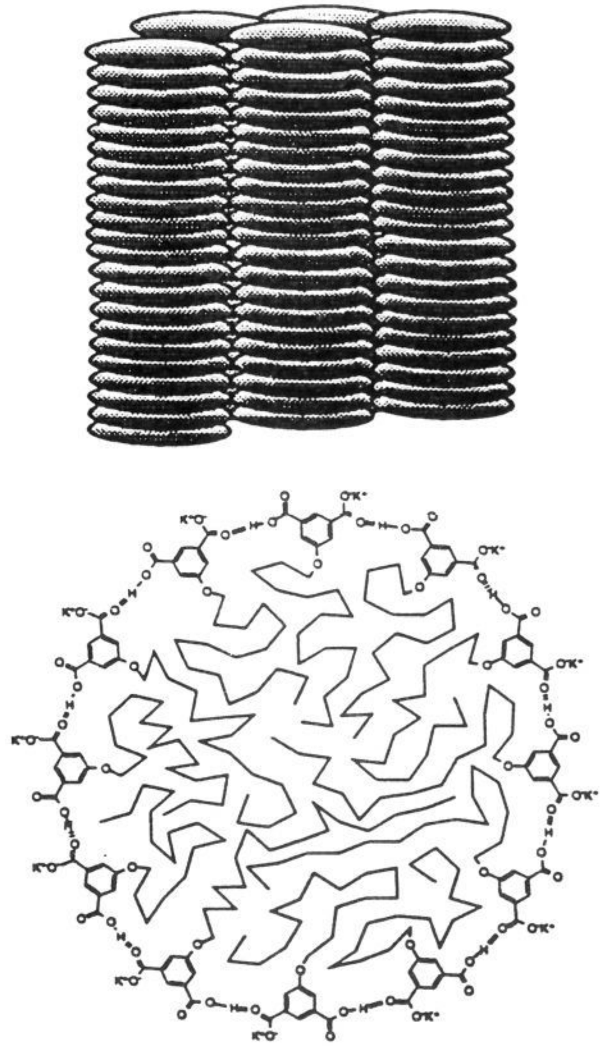

Figure 5. Disk model for fiber formation. The disks are idealized and need not be as flat as implied in the schematic.

The organic whiskers, with their remarkable length-to-width ratios, exemplify the synthesis of an interesting state of matter *via* the rational positioning of noncovalent bonding.[4]

Acknowledgment. This work was supported by the Army Research Office. The electron microscopy was supported in part by NIH Grant RR-00165 from the National Center for Research Resources to the Yerkes Primate Center.

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(3) Lehn, J.-M.; Malthete, J.; Levelut, A.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1794. Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1134. Yamamura, K.; Okada, Y.; Ono, S.; Watanabe, M.; Tabushi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 443.

(4) For a list of references on the use of hydrogen bonding for designed structures, see footnote 5 in the following: Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941.