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## Chiral Selection When Stirred, not Shaken

I AM PUZZLED BY THE REPORT THAT THE chirality of aggregates of certain porphyrin derivatives can be influenced by the direction of turning the solution in a rotary evaporator, put forward by J. M. Ribó and coauthors (Reports, "Chiral sign induction by vortices during the formation of mesophases in stirred solutions," 15 Jun., p. 2063). I have always worked under the assumption that the ordinary laws of thermodynamics and kinetics apply rigorously to the asymmetric selectivity of any process.

The results reported—a consistent 85% statistical bias in the chirality of porphyrin aggregates—would seem to require that one aggregation initiation step (essentially a crystal seeding) have about a 5-kilojoule-permole higher free energy than its opposite enantiomer. What could the source of such an

energy difference possibly be? The rotation frequency, about 10 hertz, or the maximum linear speed of the rotating solution, about 1 meter per second, is many orders of magnitude below the energy difference that is needed between the two chiralities of aggregates in the initiation step.

Chirality necessarily involves three dimensions. Surface effects could conceivably provide the energy bias needed in the third dimension. There has to be some mechanism to concentrate the exceedingly diffuse chiral bias energy of the entire system to a chemically significant level in a microscopic domain to produce any

real statistical effect.

DONALD S. MATTESON

Anticlockwise vortex motion

Vo
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## Response

## **OUR RESULTS CANNOT BE INTERPRETED IN**

terms of a symmetry breaking exerted by an external polarization (such as asymmetric induction or asymmetric amplification). In this case—that is, in the typical context of organic chemistry reactions—the arguments raised by Matteson would be valid, and the asymmetric induction or chirality selection would be understood within the classical analysis of the coordinate reaction model.

Conversely, our scenario, by no means in contradiction with thermodynamics, corresponds to a spontaneous symmetry breaking process—a far-from-equilibrium cooperative phenomenon that takes place during an

Vortex motion as a chiral force. In aqueous solution, zwitterionic porphyrin molecules spontaneously assemble into stacks as a result of electrostatic and hydrogen-bonding interactions. These aggregates then assemble into supramolecular fiberlike structures that are helically oriented in the direction opposite to the vortex motion.

## 80% increase in impact factor (2000: 1.798)

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aggregation process in a nonhomogeneous system. In these nonequilibrium situations, symmetry breaking can occur as a consequence of weak stochastic fluctuations coupled with an autocatalytic process. In the absence of any external polarization, the chirality sign of the supramolecular structures formed during this aggregation process is determined by chance and the "racemic order" would be achieved after a large enough number of experiments. This perfectly symmetric bifurcation situation is, however, modified in our case. Our results strictly point out that the direction of the stirring vortex, a weak external polarization force, selects the chirality sign of these aggregates, introducing a bias on the otherwise random selection due to stochastic fluctuations. Moreover, this is also an example of how information can be exchanged between the molecular and macroscopic levels in the self-assembly of hierarchical structures in processes governed by nonlinear effects out of thermo-

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dynamic equilibrium.

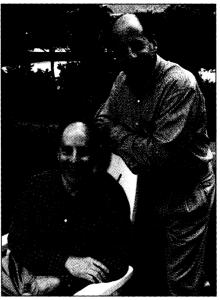
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#### **CORRECTIONS AND CLARIFICATIONS**

**REPORTS:** "A transcriptively active complex of APP with Fe65 and histone acetyltransferase Tip60" by X. Cao and T. C. Sudhof (6 Jul., p. 115). The second word in the title was incorrect. The title should have been "A transcriptionally active complex of APP with Fe65 and histone acetyltransferase Tip60."

**REPORTS:** "Cooperation and competition in the evolution of ATP-producing pathways" by T. Pfeiffer, S. Schuster, and S. Bonhoeffer (20 Apr., p. 504). Two mistakes were made in parameters that affect information in note 27 and figure 1. First, in note 27 the probability with which resource is added to a site is 0.00005 instead of 0.0005. Second, all diffusion rate constants need to be divided by 4; thus,  $D^N$  in both instances in the legend to figure 1 should have been 5 instead of 20, and the values for  $D^N$  along the z axis in figure 1C should have been 5, 3.75, and 2.5 instead of 20, 15, and 10, respectively. In addition, the diffusion rate constant  $D^{S}$  in note 27 should have been 0.25 instead of 1.

**NEWS FOCUS:** "Twin stars of astrophysics make room for two" by M. Sincell (10 Aug., p. 1040). In this profile of astrophysicists Fred and Don Lamb, the caption to the accompanying photograph (reprinted here) misidentified the brothers. Fred is on the left and Don on the right. *Science* deeply regrets the error



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