

The Origin of Chirality in the Molecules

In the last couple of years we

have witnessed the publication of a few monographs describing the current knowledge, theories, and proposed experiments to account for the origin of molecular chirality.^[1,2] This excitement reflects our passionate interest in solving one of the most important questions of contemporary science, which we have invariably linked to the origin of life on earth. However, as Jay Siegel once wisely pointed out, the existence of molecular asymmetry in the universe does not constitute a biogenic signature per se,[3] although it is true that life, at least as we know it, is inherently chiral. There are numerous hypotheses and different scenarios aimed at solving this fascinating conundrum—certainly a confusing situation, both for newcomers and for those already familiar with the field. Naturally, many of the proposed models can be rejected immediately, including examples of postulated asymmetric synthesis and asymmetric amplification, which fail because they are incompatible with credible prebiotic conditions. Failure to meet this criterion even disqualifies the Soai reaction (autocatalytic addition of dialkylzinc to 2-alkynylpyrimidyl aldehydes, usually carried out in hydrocarbon solvents), which is a nearly perfect case of asymmetric autocatalysis that is capable of producing, within a few cycles, almost enantiopure products starting from a tiny enantiomeric excess of the initial catalyst. Although the Soai reaction has no prebiotic connection in terms of experimental conditions or substrates, its intellectual appeal rests on the possibility that symmetry breaking might have taken place through asymmetric autocatalysis and, moreover, that a chiral bias can be induced in combination with a weak external chiral physical field or a chiral initiator in minute amounts.

To continue the above analysis, one welcomes the last and shorter publication (only 150 pages) in this saga of monographs: The Origin of Chirality in the Molecules of Life, which contains the important words revision and perspectives in the subtitle. The volume is co-authored by Professors Albert Guijarro and Miguel Yus of the University of Alicante. Guijarro is a young researcher who developed an interest in the fundamental aspects of the origin of chirality during his post-graduate studies, and Yus is a well-known leading expert in synthetic methodology and stereoselective reactions. The book is divided into nine chapters, which vary in length and degree of rigor. It benefits from the fact that it is the work of only two authors, thus providing a concise and unifying approach.



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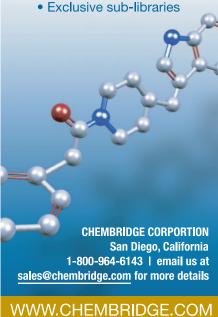
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The introductory remarks and historical journey (Chapter 1) begin, as expected, with Biot, Pasteur, and other researchers who developed precise solutions to the puzzle of quartz and tartrate crystals. However, this appetizer ignores the early work on tetrahedral carbon, a structural aspect that underpinned a radical transformation in chemistry and led the way to an understanding of stereo-isomerism and optical activity. Chapter 2 gives the reader a quick introduction to chance and deterministic theories of biomolecular chirality, so that he or she can more fully appreciate the nature of the racemic state, as well as the statistical aspects when homochiral polymerization is considered within an evolutionary context. I enormously enjoyed reading this chapter, even though specialists might like to have a more comprehensive account of developments.

Chapters 3 and 4 discuss the concept of chirality and chiral physical forces, respectively. I found this sequence to be particularly useful and didactic, as the former describes the so-called discrete symmetries (charge conjugation, parity, and time reversal) followed by the concepts of true and false chirality that were introduced by Barron, and explains how they have proven to be useful in assessing the feasibility of absolute asymmetric syntheses under electric and magnetic fields. Chapter 4 goes on to describe other cases of true chirality such as photolysis with circularly polarized light, magnetochirality, and vortex motion. This chapter also includes a preliminary excursion into the Standard Model of elementary particles, the electro-weak theory, and parity violation. These subsections are quite understandable, although the background is not an introductory read. You could be confused, for example, if you do not already know a little about symmetries and conservation laws in quantum theory. In this context, it would also have been useful to mention the classical Hund's paradox. formulated at the beginning of the quantum era, which considers a degenerate two-state system that appears to contradict the existence of optical isomers. Introducing a parity-violating term into the Hamiltonian would result in two enantiomeric states becoming true stationary states.

The authors then walk the reader through a noteworthy Chapter 5 that discusses the well-known amplification mechanisms, autocatalysis, and nonlinear effects. It is pleasing to find that, in the light of recent experiments, Guijarro and Yus have incorporated a section on eutectic mixtures and their role in asymmetric crystallization and sublimation, including serine clusters that can only be detected by electrospray ionization.

Chapter 6 (entitled "Spontaneous Symmetry Breaking", rather confusingly as the concept has already been introduced and used earlier) concentrates on asymmetric crystallization, especially of NaClO₃. Chiral crystals and chiral faces are treated again in Chapter 8, with a focus on their putative role in the emergence of prebiotic homochirality. Here the authors also briefly introduce the fascinating case of self-assembly at the air–water interface, which leads, for example, to the generation of homochiral oligopeptides (as remarkably demonstrated by Lahav and associates). The preceding Chapter 7 deals with exochirality: meteorites and comets as reservoirs of chiral organic substances, providing evidence of nonracemic conditions in the universe.

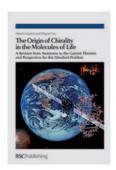
The concluding chapter, "Intrinsic Asymmetry of the Universe", represents a valuable epilogue in the search for a plausible answer to this unsolved problem, the leitmotiv traced by the authors from the beginning of the book. As Guijarro and Yus note, the observed asymmetry is most likely linked to the prevalence of matter over antimatter. The topic is exciting, as evidenced by the award of the 2008 Nobel Prize in Physics for further advances in understanding the phenomenon of spontaneous symmetry breaking. Again, the subject is not trivial, as the breaking of symmetry is probably connected with the masses of the "up" and "down" quarks as well as other formalisms that require the aid of quantum chromodynamics. Chapter 9 is attractive enough in itself, but it is also distracting, as the authors move backward to concepts and ideas (CP violation, the Standard Model, etc.) already introduced in Chapter 4.

In spite of some criticisms, as discussed above, the book is remarkable and should be extremely useful, especially for advanced students starting in this multidisciplinary field, or for lecturers to use in their seminars. The book is nicely illustrated and contains a valuable list of references at the end of each chapter. Its beauty lies in that it does not get bogged down in details, critical and accurate though they are. I recommend librarians to acquire this book, which should also find a place on the desks of interested researchers and educators. The Origin of Chirality was a joy to read; bravo to authors Guijarro and Yus.

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to the Current Theories and Perspectives of this Unsolved Problem. By Albert Guijarro and Miguel Yus. Royal Society of Chemistry, Cambridge 2008. 150 pp., hardcover £ 65.00.—ISBN 978-0854041565

^[1] G. H. Wagnière, On Chirality and the Universal Asymmetry. Reflections on Image and Mirror Image, Wiley-VCH, Weinheim, 2007; book review: Angew. Chem. Int. Ed. 2007, 46, 9143–9144.

^[2] U. Meierhenrich, Amino Acids and the Asymmetry of Life, Springer, Dordrecht, 2008.

^[3] J. S. Siegel, Chirality 1998, 10, 24-27.