Amino Acids and the Asymmetry of Life

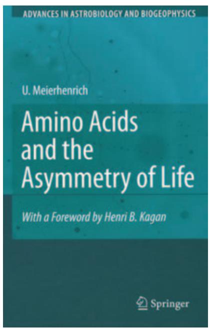
Amino Acids and the Asymmetry of Life, by Uwe Meierhenrich, is part of a series entitled *Advances in Astrobiology and Biogeophysics*. Much of the book deals with single chirality in amino acids and the questions of how and where the selectivity for one enantiomer over the other might have arisen. The "where" aspect logically includes an extensive discussion of amino acids and other organic compounds found in meteorites and comets. The discovery that some of these amino acids, particularly (unnatural) α-methylated ones, have appreciable enantiomeric excesses has led to increased interest in extraterrestrial sources of organic materials as possibly having a role in the process of the origin of life. The extraterrestrial models have received further support from the observation that mixtures of simple molecules such as H_2O, NH_3, CO_2, and CH_3OH observed in space and exposed to irradiation on ice crystals or dust particles can generate more complex organic compounds, including amino acids. One can imagine such reactions taking place on a large scale on suitable comets. Clearly, it would be of great advantage to study a comet directly rather than having to depend on the often damaged and contaminated organic material from meteorites. In this context, the author of the book describes the ROSETTA mission launched by the European Space Agency in 2004 from the vantage point of his own involvement, particularly in the Cometary Sampling and Composition Experiment (COSAC), in which enantioselective gas chromatography and mass spectrometry will be used to analyze and measure enantiomeric excesses of amino acids and to detect other organic compounds on the Churyumov–Gerasimenko comet. The experimental challenge of making derivatives that are volatile enough to be analyzed (after collection, a technically highly complex task), without solvent, in a capsule under extreme conditions on the surface of a comet, is daunting. That challenge and the technical details thereof are described professionally and with verve. The opportunity to do chemistry is limited in the extreme. The *only* chemical reaction that can be carried out in this space-lander is esterification of acids with dimethylformamide dimethylacetal (DMF-DMA). If all goes well—including, for example, that the reagent DMF-DMA and the coatings of the chiral columns survive the trip—these experiments will take place in 2014 (!) after the space-lander has successfully established itself on the surface of the comet.

The author also discusses the current status (space programs are famous for change owing to funding problems and political factors) of an ExoMars mission planned for launching in 2013. The on-board laboratory for analysis of organic compounds will also allow the possibility of carrying out hydrolyses to decompose macromolecules into lighter constituents. On the basis of earlier Viking experiments, it was concluded that there were no organic compounds in the material sampled on the surface of Mars. This conclusion was later vigorously contested. An extensive new search for organic compounds will be made in the ExoMars mission with the aid of the far more sophisticated on-board laboratory that is well described in this book.

This information about the ROSETTA mission now in progress and the planned Mars mission is placed in the context of a broader discussion about how amino acids might be formed and possible mechanisms for the inducement and amplification of a single enantiomer. Earth gives us, of course, a world of life with single chirality. Although we will probably never know exactly how this came about, it is essential in the context of chemical evolution to discover and understand mechanisms that can lead to single chirality, and to demonstrate to ourselves that single chirality is a logical consequence of the subsequent evolution. One naturally has to take extraterrestrial matter into account in the development of theories. The information forthcoming from exploration of planets and comets will clearly be of great use. On the basis of structures of organic compounds already isolated, interesting speculations can be made. Various diamino acids (for example, 2,3-diaminopropanoic acid) have been discovered in meteorites, and it has been suggested that these could serve as a peptide backbone of a "pre-RNA". Although speculative, these models give much food for thought.

The author also provides, at the beginning of the book, an overview of the chemistry and stereochemistry of amino acids. After an introduction to stereochemistry as applied to amino acids, there is a brief discussion of the function of amino acids in living organisms. The book then turns to mechanisms on earth that could have delivered single chirality. Crystallization on minerals is considered, the effects of the weak nuclear interaction are discussed, and the possible influence of light and other forms of radiation, as well as chiral fields, is analyzed. The book ends with a discussion—including the necessary mathematics—of autocatalytic amplification mechanisms that could translate a small enantiomeric excess into a very large one.

The range of subjects is thus fairly large, and the discussion is for the most part informative but not deep. On occasion the information with regard to chemistry is misleading or of debatable value. This reviewer was struck by three particular examples. First, the highly pertinent Soai reaction discussed in



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the final chapter is a marvelous example of how autocatalysis on even a tiny enantiomeric excess can lead to enantiomeric near-purity. The chemical mechanism of this autocatalytic reaction was first uncovered by Blackmond and Brown, who unfortunately are not even cited. Second, an extensive discussion of the history of the discovery of the chiral aspects of weak nuclear interactions adds little substance to such a short book. Third, the author devotes a considerable and disproportionate amount of attention to a claim that D- and L-tyrosine have inherently different solubilities, and less space to the convincing evidence disproving that claim. In a series of meticulous experiments, Lahav and colleagues showed that, as expected from everything we know about stereochemistry, there is no inherent difference in solubility, and that impurities are responsible for the apparent difference. The contributions of Lahav's group to rational and critical discussion of this and other chirality issues deserve special mention and praise in this context. However, after correctly acknowledging this evidence, the author ends this discussion with the statement: "it is not up to me to be the final judge of this scientific conflict", and offers the suggestion that the matter should be investigated further. This is unfortunate wording, as it could be perceived as reinforcing a particular opinion, in direct conflict with the precepts of the scientific method.

Effects of polarized light or other polarized electromagnetic radiation on racemates have always been found to be small, and border on the edge of reliable measurement. The effects of the weak nuclear interaction are also expected to be very small if observable at all. It is unfortunate that these very real difficulties in observation and measurement have occasionally provided a breeding ground for wishful thinking and unsubstantiated claims. The author carefully discusses a case in 1994 when it was claimed that very high enantiomeric excesses were obtained by preparing chiral alcohols from prochiral ketones in a magnetic field. The source of chiral induction was not apparent, and attempts to reproduce the work failed. This report had to be retracted amid accusations of fraud and considerable negative publicity. Such events lead to skepticism. Other examples of misinterpreted, but in no way fraudulent, observations over many years have caused further confusion. For example, there were reports that amino acids in solution with very high enantiomeric enrichment were obtained from slightly enriched solids, whereas on closer investigation this turns out to be a logical consequence of the eutectic composition of the amino acid and the phase rule. Another example is that crystallization of conglomerates can produce enantiomerically enriched or enantiopure materials. This is not a wondrous occurrence. Finally, chiral contamination is a very large problem in any experiment and, although guarantees of the absence of any chiral influences are easily written, they are very hard to substantiate on close examination (as illustrated in the case of tyrosine mentioned above). Extreme care must always be taken. It has even been strongly argued that an experiment on earth in the total absence of chiral contamination is not possible.

One needs to be careful but at the same time to have an open mind. In a publication that appeared too late for inclusion in this book (*Phys. Rev. Letters* **2008**, *101*, 178301) it was reported that spin-polarized secondary electrons from irradiation of a magnetic substrate, depending on the chirality, lead to readily measurable differences between the rates of CO bond cleavage in (*R*)- and (*S*)-butanol absorbed on an iron/nickel alloy; this again illustrates that, whatever the detailed explanation, significant effects can be observed in the proper settings. This is one of the reasons why it is so important to gain information from space missions such as those described with enthusiasm in this book.

The standard of editing of the book is indifferent. This is unfortunate, since many linguistic inconsistencies that detract from the quality and lead to potential confusion could easily have been avoided.

The book provides a nice entry into numerous aspects of chirality, many of which, on closer reading, turn out to be particularly complex and challenging. It is always necessary in this area to separate the chaff from the corn.

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