

PHOTOCHEMICAL CONCEPTS ON THE ORIGIN OF BIOMOLECULAR ASYMMETRY

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Abstract. Biopolymers like DNA and proteins are strongly selective towards the chirality of their monomer units. The use of homochiral monomers is regarded as essential for the construction and function of biopolymers; the emergence of the molecular asymmetry is therefore considered as a fundamental step in Chemical Evolution. This work focuses on physicochemical mechanisms for the origin of biomolecular asymmetry. Very recently two groups, one from Allamandola at NASA Ames and the other from our Inter-European team, demonstrated simultaneously the spontaneous photoformation of a variety of chiral amino acid structures under simulated interstellar conditions. Since both groups used unpolarized light for the photoreaction the obtained amino acids turned out racemic as expected. The obtained experimental data support the assumption that tiny ice grains can furthermore play host to important asymmetric reactions when irradiated by interstellar circularly polarized ultraviolet light. It is possible that such ice grains could have become incorporated into the early cloud that formed our Solar System and ended up on Earth, assisting life to start. Several lines of evidence suggest that some of the building blocks of life were delivered to the primitive Earth via (micro-) meteoroids and/or comets. These results suggest that asymmetric interstellar photochemistry may have played a significant part in supplying Earth with some of the enantioenriched organic materials needed to trigger life. The search for the origin of biomolecular homochirality leads to a strong interest in the fields of asymmetric photochemistry with special emphasis on absolute asymmetric synthesis. We outline here the theoretical background on asymmetric interstellar ice photochemistry, summarize recent concepts and advances in the field, and discuss briefly its implications. The obtained data are crucial for the design of the enantioselective COSAC GC-MS experiment onboard the ROSETTA spacecraft to a comet to be launched in the very near future.

Keywords: absolute asymmetric synthesis, asymmetric photochemistry, amino acids, asymmetric photolysis, comet, Cosac, cosmic dust cycle, interstellar dust, interstellar medium, leucine, Rosetta

1. Introduction

The essential step within the process of the evolution of life is clearly the emergence of biomolecular homochirality. Several controversial theories have been developed to explain an abiogenic origin of the biomolecular chiral purity in terms of the physicochemical processes involved. The theories have been classified by Bonner (1991) into random mechanisms on the one side and determinate mechanisms on the other side. Random mechanisms are undirected processes that lead to the appearance of biomolecular asymmetry by mere chance. The spontaneous



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chiral symmetry breaking observed in autocatalytic systems serves as an example (Kondepudi and Asakura, 2001). Determinate mechanisms involve the interaction of racemic or prochiral substances with chiral physical driving forces, which cause the prevalence of one enantiomer. Examples of such mechanisms include the adsorption on enantiomorph surfaces of quartz (Soai *et al.*, 1999) or calcite (Hazen *et al.*, 2001), the directed vortex (Ribó *et al.*, 2001), the weak force (Yamagata, 1966), spin-polarized electrons (Musigmann *et al.*, 1999), and circularly polarized light (CPL; Kuhn and Braun, 1929; Kuhn and Knopf, 1930). New concepts and results reviewed by Griesbeck and Meierhenrich (2002) particularly on the absolute asymmetric synthesis induced by photochemical reactions are encouraging and will be outlined here. The photochemistry of the origin of life, particularly both the symmetric and asymmetric photoformation of any precursor molecules under simulated conditions of chemical evolution, and the emergence of the biomolecular homochirality will be discussed.

2. Ice Photochemistry in Simulated Interstellar Environments

Amino acids are the chiral building blocks of proteins and certainly played a key role in both the appearance of life and the emergence of biomolecular asymmetry on Earth. The proteins of living organisms are composed of 20 basic amino acids. It is thought that certain amino acids had already been present when life appeared nearly four billion years ago. At that time, they could have been formed in the Earth's atmosphere and/or in the ocean's hydrothermal systems. As some of these amino acids were discovered in carbonaceous meteorites, a significant contribution of extraterrestrial amino acids synthesized in interstellar environments and delivered to Earth in the form of cometary dust offers an attractive alternative to a purely terrestrial origin of life on Earth.

To support this hypothesis, a mixture containing ice crystals of water, ammonia, methanol, carbon monoxide and carbon dioxide was irradiated at the Leiden Observatory for Astrophysics (Netherlands), in conditions that simulated those found in interstellar space (high vacuum chamber at $-261\text{ }^{\circ}\text{C}$) (Mendoza-Gomez and Greenberg, 1991). After heating the samples to room temperature, the residue was analysed at the CNRS Centre de Biophysique Moléculaire in Orléans (France) by enantioselective gas chromatography coupled with mass spectrometry (GC-MS). 16 amino acids, six of which are among the 20 protein-constituent amino acids (glycine, alanine, valine, proline, serine, and aspartic acid), were identified (Muñoz Caro *et al.*, 2002). The results were simultaneously confirmed by Bernstein *et al.*, (2002) of NASA Ames. Besides amino acids a number of photochemically produced other organic molecules was identified in simulated interstellar environments (Meierhenrich *et al.*, 2001d; Muñoz Caro *et al.*, 2003). The obtained data on the identification of α -amino carboxylic acids are corroborated by the detection of

amino acids extracted from samples of meteorites (Engel and Macko, 1997; Cronin and Pizzarello, 1997).

The data strongly imply that photochemical reactions take place on small ice grains that develop in the interstellar medium. Interstellar dust particles in dense clouds accrete ice mantles. As seen in infrared (IR) observations, this ice layer consists mainly of water ice, but also carbon and nitrogen containing molecules. Dust particles then coagulate forming larger bodies like comets. The products of photochemical reactions could be preserved in these bodies, and in term be delivered to the Earth during the heavy bombardment geological period which ended about 3.8 Gyr ago.

The detection of circularly polarized electromagnetic radiation in interstellar environments was reported first by Bailey (1998) and was confirmed by further investigations. The interstellar asymmetric light source was discussed to be produced by dust grains aligned by a magnetic field in the reflection nebulae in star formation regions and to be responsible for enantiomeric selection of interstellar organic molecules (Bailey, 2001). The topical discussion focuses on the exact asymmetric photochemical mechanism and on the molecular pathway – e.g. via chiral amino acids or via ribose molecules – for any interstellar processes concerning a potential enantiomeric enrichment (e.g. Cerf and Jorissen, 2000; Jorissen and Cerf, 2002).

3. Enantiomer Separations by the Cometary Mission ROSETTA

In search for the hypothetical influence of asymmetric photochemistry in chemical evolution an *in situ* determination of enantiomeric excesses in extraterrestrial objects has become part of space scientific programs. Today, the measurement of enantioenrichments is included for the first time in one of the cornerstone missions of the European Space Agency ESA and the Max-Planck-Institut für Aeronomie in Katlenburg-Lindau, Germany. This program, the cometary mission ROSETTA was designed and constructed in order to identify chiral organic molecules *in situ* on the surface of a comet and to determine values of enantiomeric excesses therein.

A cometary nucleus is believed to consist of a conglomerate of silicate grains surrounded by a mantle of H₂O, CO₂, CO, and other ices which may serve as a matrix for many kinds of atoms and molecules (Greenberg, 1993). So far, the accurate chemical and chiral composition of a cometary nucleus is unknown. Due to the results of laboratory simulation experiments, we have good reasons to assume that specific chiral organic molecules like amino acids can be found in cometary matter.

The ROSETTA Orbiter will be launched in the very near future in order to deliver the small subsatellite ROSETTA Lander RoLand to a comet, which is planned to detach from the orbiter and to land on the cometary surface. RoLand's Cometary Sampling and Composition Experiment COSAC is designed to identify complex organic molecules and to search for potential enantiomeric enhancements

in cometary matter (Thiemann *et al.*, 2001c; Meierhenrich *et al.*, 2001e, 2003a). In the case of success of this mission we would be able to specify the extraterrestrial precursors of life based on chiral carbon chemistry in its prebiotic forms.

The development of the COSAC hardware is ultimately finalized (Rosenbauer *et al.*, 2002). In order to analyse the cometary sample with respect to its chemical and enantiomeric composition *in situ* the material will be heated to transform the solid material into its gaseous phase. The heating process will be accomplished in small ovens into which the sample has been injected by RoLand's Sample Drill and Distribution Subsystem. The ovens will be mounted on a 'carrousel' and moved by rotation, from a position where the sample will be filled in, to the so-called 'tapping station', where the ovens are going to be closed and heated stepwise to levels programmable by ground commands. The pressure developed during each heating step will be measured and recorded too, because it is indicative of the total amount of gas released. The more polar analytes (of poorer volatility) can be alternatively transformed into volatile components by a special development of a gas phase derivatization technique (Thiemann and Meierhenrich, 2001b; Meierhenrich *et al.*, 2001b). The analytes in the gaseous phase will be transferred onto a suitable capillary column coated with chiral (Figure 1) as well as non-chiral stationary phases. The chromatographically separated analytes are going to be detected, identified, and quantified on miniature thermal-conductivity detectors TCDs, which are coupled with a multi-reflectron TOF mass spectrometer.

Chiral stationary Chirasil-Val and cyclodextrin based phases suitable to perform enantioselective gas chromatography and applicable to a wide range of chiral organic compounds (Meierhenrich *et al.*, 1999) including alcohols, diols (Thiemann and Meierhenrich, 2001a), amino acids, hydroxy carboxylic acids, and even hydrocarbons (Meierhenrich *et al.*, 2001c, 2003b) were therefore developed and studied in the laboratory. The gas chromatographic *in situ* separation of enantiomers allows the quantification of specific enantiomers of cometary material and thus the determination of enantiomeric excesses which, should they be found, might contribute to the understanding of the phenomenon of enantiomeric asymmetry of biomolecules on Earth.

4. Photochemical Origin of the Biomolecular Asymmetry

Already as early as in 1929, irradiation of racemic or prochiral precursor molecules with circularly polarized light was a proposed scenario for the origin of biomolecular asymmetry (Kuhn and Braun, 1929; Kuhn and Knopf, 1930). With the aim to investigate and verify photochemical theories for the induction of biomolecular homochirality via electronically excited states, our topical research focuses on the effect of circularly polarized light (CPL) on racemic organic molecules. Predominantly, for the photochemical formation of optically active molecules

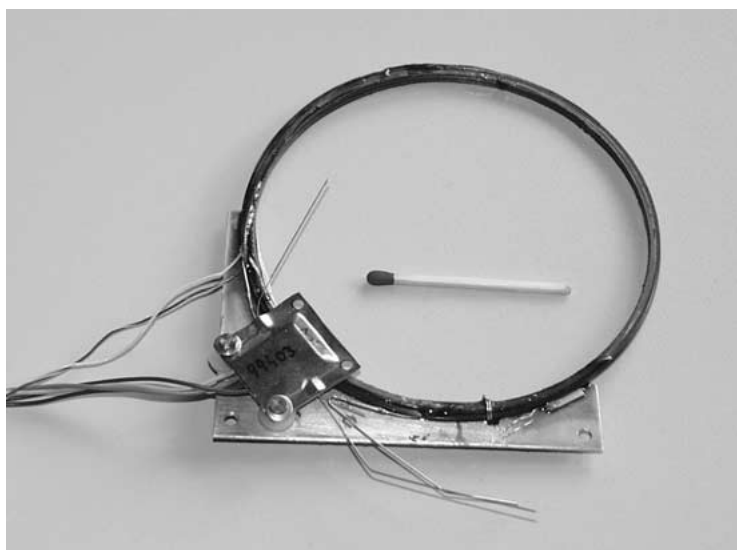


Figure 1. Mechanically fixed capillary column before implementation into the COSAC multi-column gas chromatograph oven with installed filament heating system and micro thermo conductivity detector TCD equipped with the chiral stationary phase *Chirasil-L-Val* [10 m \times 0.25 mm (inner diameter), 0.12 μ m (film thickness), Varian-Chrompack]. In parallel, chiral *Cyclodextrin G-TA* (10 m \times 0.25 mm, 0.125 μ m, Astec), *Chirasil-Dex CB* (10 m \times 0.25 mm, 0.25 μ m, Varian-Chrompack), and 5 achiral stationary phases (cf. Szopa *et al.*, 2002) were mounted in the COSAC GC. Credit: Max-Planck-Institut für Aeronomie.

in non-racemic yields one distinguishes between *enantioselective photolysis* and *absolute asymmetric photosynthesis* (Griesbeck and Meierhenrich, 2002).

To establish the most suitable conditions for the enantioselective photolysis, electronic transitions of leucine were studied in the VUV photon range. Leucine was chosen as the target for asymmetric decomposition experiments for three reasons. First, the photochemistry of leucine is well known for its prominent (π^* , n)-transition. Second, leucine has the largest g factor in proteinaceous amino acids (Flores *et al.*, 1977). Investigations on enantioselective photodestruction of racemates emphasize the importance of the anisotropy factor g ($g = \Delta\varepsilon/\varepsilon$). The enantiomeric purity achievable during photolysis of a racemate is a function of the magnitude of g and the extent of reaction (Balavoine *et al.*, 1974). Third, enantiomer separation techniques provide high separation factors α and resolutions R_S for leucine.

In a first step, absorption spectra of solid films of leucine were measured between 110 and 220 nm by absorption spectroscopy at beamline SA-61 of the French synchrotron facility *Laboratoire pour l'Utilisation du Rayonnement Électromagnétique* LURE in Paris. The (π^* , n)-transition of leucine was observed at 211 nm, its (π^* , π_1)-transition at 183 nm, the tentative (π^* , π_2)-transition at 142 nm and its potential (σ^* , σ)-transition below 120 nm (Figure 2). Enantiose-

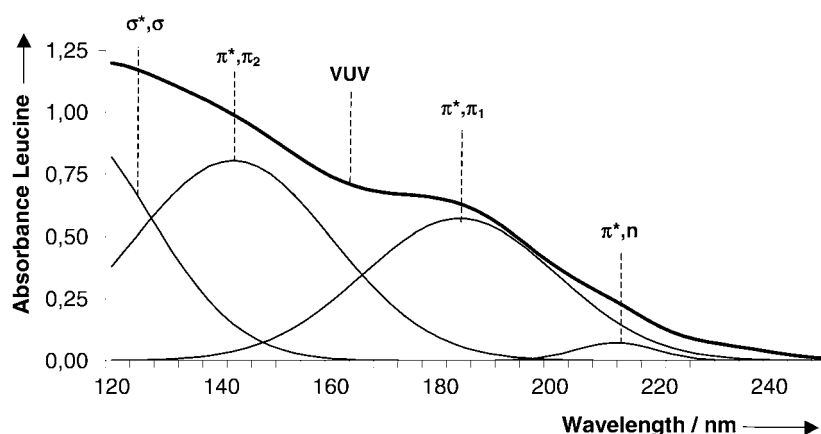


Figure 2. Absorption spectrum of the amino acid leucine in the vacuum ultraviolet range, recorded in a solid sample film with synchrotron radiation in LURE, Paris. Maxima of electronic transitions were calculated from the VUV-absorption spectrum. Assignments of electronic transitions were obtained from theoretical data. The (π^*, n) -electronic transition was recorded at 211 nm, (π^*, π_1) -electronic transition @ 183 nm, and (π^*, π_2) -electronic transition @ 142 nm.

lective photodecomposition of leucine can be considered to be sufficiently active precisely at each of the determined electronic transition energies (Boillot *et al.*, 2000).

In order to determine in a second step the direction of the possible enantiomeric excess, chiroptical investigations on amino acids were taken into account. Circular dichroism (CD) spectra of (*L*)-leucine show a maximum of molar ellipticity Θ [$\Theta = 3300(\varepsilon_L - \varepsilon_R)$, with dichroic absorption $\varepsilon_L - \varepsilon_R$] for the (π^*, n) -transition, a minimum for its (π^*, π_1) -transition, and probably a second maximum for the (π^*, π_2) -transition (Figure 3). Based on this observation one can infer that the (π^*, n) -transition of (*L*)-leucine is caused preferentially by left circular polarized light (*l*-CPL), the (π^*, n) -electronic transition of (*D*)-leucine by *r*-CPL and so on. Therefore, at the 211 nm (π^*, n) -transition *l*-CPL is assumed to result in an enantiomeric excess (e.e.) of (*D*)-leucine, at the 183 nm (π^*, π_1) -transition *l*-CPL should lead to an e.e. of (*L*)-leucine, and so on. By the use of *r*-CPL inverse enantioenrichments are expected. The observed wavelength-shift between the VUV- and the CD-data cannot be explained certainly at present.

To achieve enantioselective photodecomposition, finally, the newly developed polarizing undulator *Ophelie* installed in the Super-ACO storage ring at LURE was employed for the first time as a source of circularly polarized synchrotron radiation (SR) in the VUV to irradiate the samples at various wavelengths owing to the SR tunability, and with circular polarization rates above 92% in the 6–10 eV range. This irradiation was provided for the SU-5 beamline with the energy of the circular polarized synchrotron radiation first set to 6.9 eV and, second, to 7.3 eV, closely matching the desired 183 nm (π^*, π_1) -transition. Solid films of (*D*, *L*)-

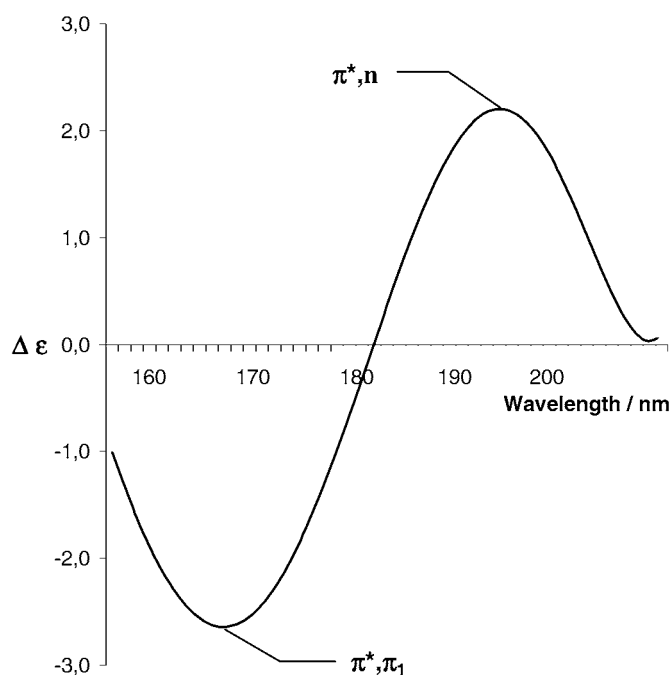


Figure 3. Circular dichroism spectrum of the amino acid (L)-leucine as zwitterions in hexafluoroisopropanol taken from Snyder *et al.* (1973). The (π^*, n) -transition of the carboxylate anion is magnetically allowed and electrically forbidden; the (π^*, π_1) -transition is magnetically forbidden and electrically allowed.

leucine were deposited onto MgF_2 windows using film thicknesses between 2 and 10 μm and irradiated with right and left circularly polarized SR. During irradiation the ‘global’ photodecomposition process was followed by measuring the increase of transmission of the films from e.g. 16% to 54%. After a photodecomposition of about 70% of the starting material the irradiation process was stopped. Due to different molecular absorption coefficients of the two leucine enantiomers the highest obtained enantiomeric excesses in the residues were found to be $\pm 2.6\%$. Analyses were performed by enantioselective capillary electrophoresis and enantioselective gas chromatographic techniques (Meierhenrich *et al.*, 2001a).

On the other hand, the pure *absolute asymmetric synthesis* of optically active molecules in nonracemic yields induced only by CPL has remained a task difficult to achieve. 30 years ago, photocyclization of alkenes in solution, performed in the presence of iodine, led to the formation of various polyaromatic hydrocarbon molecules. By irradiation with CPL chiral hexahelicene was synthesized with optical yields below 2% (Moradpour *et al.*, 1971; Bernstein *et al.*, 1972, 1973). Until today, analogue experiments have not been performed successfully in the case of amino acids or ribose molecules, i.e. of chiral structures with crucial functions during chemical evolution.

5. Outlook

The implication of our studies on the origin of biomolecular asymmetry is far reaching. The spontaneous formation of chiral organic molecules like amino acids in interstellar environments implies – since we know that circular polarized electromagnetic radiation is available and present in the interstellar medium, too – that physicochemical processes inducing the biomolecular asymmetry may have occurred not only on Earth but in interstellar environments as well. Future projects will investigate this hypothesis by studying the specific function of the identified amino acids in the simulated interstellar medium during chemical evolution. Additionally, we will try to determine the exact temperature and mechanism at which amino acids structures form under interstellar conditions. Our interest is focussed on the precursor molecules of amino acids before acid-mediated hydrolysis. We collaborate with astronomers with the aim of a direct identification of amino acids in the interstellar medium which was so far not possible. Collaboration was already started with the *Institut Astrophysique Spatiale* IAS in Paris, France, in order to study the photoformation of chiral amino acids under simulated interstellar environments. Enantiomeric excesses are assumed to build up through irradiation with circularly polarized synchrotron radiation directly via an enantioselective photochemical absolute asymmetric synthesis. Finally, as outlined above we look forward to receive the data on enantiomer separation by the COSAC-Experiment onboard ESA's mission ROSETTA to a comet.

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