

On the Origin of “Pure” Chirality of Aminoacids and Saccharides at the Prebiotical Stage

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Abstract. Possible explanation is offered for the origin of pure chirality of aminoacids and saccharides of racemic compounds during the prebiotical stage of evolution. It is based on the theory of “noise induced phase transitions”, a mechanism approached in previous years by synergetic methods. It follows from this approach that a sufficiently intensive noise in the environment of the formation of racemic compounds of L- and D-chiralic macromolecules could produce homochiralic state, i.e. a state with either pure L- or D-chirality.

Key words: Chirality — Homochirality — Evolution — Fluctuation — Noise

Introduction

The question concerning the origin of optically active molecules in nature is closely associated with the origin of life itself. It is well known that chiralic molecules are the most important structural units of living organisms, these molecules exhibit one of two possible symmetrical forms. Thus, all aminoacids which make up proteins are purely L-chiralic while saccharides forming the basic units of polysaccharides and nucleotides are exclusively D-chiralic. This fact has been the subject of numerous considerations and qualitative and quantitative analyses. The problem is that spontaneous synthesis of these molecules under laboratory conditions always results in the generation of optically inactive racemic compounds, i.e. in a system with equal numbers of L- and D-chiralic molecules, because this state is thermodynamically most acceptable. In prebiotic era this symmetry had to be broken to allow homochirality to arise. Mechanisms which could have resulted in absolute suppression of chirality of one type and absolute preference of chirality of the second type at the same time, are subject of discussion.

One of the most significant attempts to explain this symmetry breakdown has been based on the known phenomenon of parity violation at weak interactions.

(Ulbricht 1975). β -radiation emitted at radioactive decay does not keep the mirror symmetry and it selectively affects macromolecules with L- and D-chirality. Considering that the atmosphere of our planet at those times was considerably radioactive about 20% of the total energy on the earth surface is assumed to have been a product of β -radioactive nuclei decay (Kovacs 1981) - it can be expected that there was an abundance of appropriate electrons for prebiological chemistry. The arising biosphere homochirality thus could have been principally stimulated by β -radiation interactions with the respective macromolecules. This process could have been occurring also in cosmic space (it is not surprising that breakdown of chirality symmetry was observed in molecules of meteoritic origin), and this gives a chance to find the origin of life in the universe (Hoyle and Wichramasinghe 1979). However, any version about the extraterrestrial origin of life is only a transfer of the problem to other planets.

Though sequences of aminoacids reminding prebionts and archebionts were discovered in some meteorites, pure optical activity was observed in no case (Hayes 1967; Kvenvolden et al. 1971; Miller et al. 1976, Ferrara et al. 1977). Analysis of the samples from Mars and the ones from moon dust brought by "Apollo" have led to the same results (Williams and Smith 1977). On the contrary, in prehistoric Earth minerals traces of optically active molecules were found (Kvenvolden et al. 1969). Many hypotheses seeking the primary reason of biosphere asymmetry were based on such phenomena as the asymmetry of earth rotation (Kovacs et al. 1981), circular polarization of sun radiation (Barron 1972), and various geophysical and geocosmical factors (for a more detailed review see e.g. Strašák 1986). Quantitative theories (of one chirality type macromolecule predominance in comparison with the opposite one) based on this mechanism have shown that such a selective effect is too weak to ensure formation of homochiralic systems in the biosphere at a reasonable time (e.g. Rein 1974; Morozov et al. 1984b). Based on these results Morozov et al. 1984a) concluded that no emerging of homochirality due to continuity of the process was possible. Symmetry breaking had to be caused by a qualitative jump, adequate to the well known processes described by the mathematical theory of catastrophes. The solutions to the problem of homochirality of macromolecules in biological systems consist probably in a synergetical approach, mainly developed in numerous books published in edition "Synergetics" (e.g. Haken 1978) as well as elsewhere. The theoretical basic for this approach is represented by the laws of non-equilibrium thermodynamics of open systems. It is characteristic for these systems that fluctuations can be considerably amplified in amplitude, time and space when below the threshold stability of a stationary state. If fluctuations reach macroscopic dimensions, the system becomes unstable and begins developing into a new non-equilibrium but stationary state characterized by minimum entropy production and limited order. It is worth mentioning that formulation of mathematical evolution equations for the racemic system of L- and D-chiralic molecules had already been

attempted in 1953 (Frank 1953). It was based on non-linear terms connected with possible mutual neutralization ("annihilation") of L- and D-molecules. From such formulation of equations follows existence of unstable homogeneous distribution and, consequently the possibility of a qualitative change towards the predominance of one chirality. In this and also in other works, fluctuations are required as a stimulus of a qualitative change; however, the fact has been ignored that the whole process of synthesis occurred in a permanently "noisy" environment. The noise could have been either classical (e.g. thermal) or of quantum character. It has been shown in recent years that noise can stimulate qualitative changes of a system and determine its properties in a new state with broken symmetry (see e.g. Horsthemke and Lefever 1984). The problem of "selection from between two equivalents" in various biological systems on the species level was thus successfully solved. It can be expected that a similar process could have occurred at the prebiotic stage involving racemic molecule compounds of L- and D-chirality. We will try to show that such a process might be realistic.

The evolution equations

Let us assume that in a certain investigated volume a process of production of macromolecules with L- and D-chirality occurred with a certain intensity, and that these macromolecules can transform mutually from one type to another and they can mutually neutralize themselves. Also, the possibility of spontaneous decay of macromolecules can be considered. The increase in the concentrations of macromolecules of both types (N_1, N_2) per unit time is supposed to be constant; considering mutual transformation, the increase is directly proportional to the concentration of the other type, and the decrease per unit time (neutralization) is obviously directly proportional to the product of respective concentrations. The decrease due to spontaneous decay is directly proportional to the concentration of the respective type. The relevant evolution equations can be written in the form

$$\frac{dN_1}{dt} = \alpha'_1 + \beta_1 N_2 - \gamma_1 N_1 - \delta' N_1 N_2 \quad (1)$$

$$\frac{dN_2}{dt} = \alpha'_2 + \beta_2 N_1 - \gamma_2 N_2 - \delta' N_1 N_2 \quad (2)$$

where $\alpha', \beta, \gamma, \delta'$ are constants.

Let us consider that a stationary state developed (within a certain time interval at least) characterized by the condition

$$N_1 + N_2 = N = \text{const.} \quad (3)$$

If a new variable x is given by the definition

$$x = \frac{N_1}{N} \quad (4)$$

equation (1) can be rewritten as follows:

$$\frac{dx}{dt} = \alpha - \beta x - \delta x(1 - x) \quad (5)$$

where $\alpha = \alpha'_1/N + \beta_1$, $\beta = \beta_1 + \gamma_1$ and $\delta = \delta'N$. The problem of "selection from between two equivalents" in the realm of biological systems at the species level (Arnold et al. 1978) yields similar equations.

Let us assume now that the processes mentioned above occur in an environment with Gaussian noise, defined by the following conditions:

$$F\{\xi_t\} = 0 \quad (6)$$

$$F\{\xi_t, \xi_{t+\tau}\} = \delta(\tau) \quad (7)$$

where F denotes the mean value of the respective quantity, ξ is the random variable, τ denotes the time interval, and δ is Dirac's function. We can imagine that the medium in which the synthesis of macromolecules of aminoacids and proteins occurred was a water solution containing organic molecules. These molecules were able to join each other at convenient mutual reorientations (in the prebiotic era) and this way generate functional units of aminoacids or proteins. Very naturally, noise in particular that generated by thermal motion could have been produced.

Random mechanical motions of organic molecules could have influenced – positively or negatively – the rate their mutual interactions toward the generation of chemical bonds. It follows from this statement that noise could have effectively influenced the processes of synthesis biological macromolecules, as expressed by the third term in equations (1) and (2). It is generally known that the influence of noise on linear terms in this equations cannot cause new qualitatively different states to arise. In general, noise can be divided into a systematic and a fluctuating part, i.e. parameter δ can be expressed in the form

$$\delta = \delta_0 + f(t) \quad (8)$$

Theoretically, the simplest variant of noise is the so called "white noise" characterized by a constant distribution of its "power" over all frequencies. In such a case, $f(t) = \sigma\xi$, where σ is the characteristic constant. Under these conditions, equation (5) gets the following form

$$\frac{dx}{dt} = h(x) + \delta_0 g(x) + \sigma g(x)\xi \quad (9)$$

where

$$h(x) = \alpha - \beta x$$

$$g(x) = x(1 - x)$$

Solution to equation (9)

The method of the solution to evolution equations containing a random variable has been proposed by many authors (e.g. in monographs by Horsthemke and Lefever 1984; Arnold and Lefever 1981). It has been based on the introduction of a density of probability of the occurrence of systems in state x at time t ($w(x, t)$), on the formulation of a relevant differential equation for this density, and on its solution. Two methods have been proposed for the formulation of such an equation: one by Ito and another one by Stratonovic. They do not differ from each other in qualitative conclusions, and since the former is a little simpler, we will use it in our further analysis. Ito's equation, corresponding to equation (9), has the form

$$\frac{\partial w(x, t)}{\partial t} = -\frac{\partial}{\partial x} [f(x)w(x, t)] + \frac{\sigma^2}{2} \frac{\partial^2}{\partial x^2} [g^2(x)w(x, t)] \quad (10)$$

where

$$f(x) = h(x) + \delta_0 g(x)$$

We are only interested in the stationary solution which is given by the function

$$w(x) = C \frac{1}{g^2(x)} \exp \left\{ \frac{2}{\sigma^2} \int_0^x \frac{f(u)}{g^2(u)} du \right\} \quad (11)$$

The system will occur in the state with a maximum density of probability. From the condition $dw(x)/dx = 0$ we obtain the general condition for the extremal state in the form

$$h(x) + \delta_0 g(x) - \sigma^2 g(x)g'(x) = 0; \quad g' = \frac{dg(x)}{dx} \quad (12)$$

In our case it is

$$\alpha - \beta x - \delta_0 x(1-x) - \sigma^2 x(1-x)(1-2x) = 0 \quad (13)$$

There is no reason to assume a systematic noise factor in further analysis, therefore we can put $\delta_0 = 0$. We assume that the system in the state without noise was racemic, i.e. $x = 1/2$. Then, the condition $\beta = 2\alpha$ must hold, so $\alpha - \beta x = \alpha(1-2x)$. The solution to equation (13) under these condition is

$$x_{1,2} = \frac{1}{2} \left\{ 1 \pm \left(1 - \frac{4\alpha}{\sigma^2} \right)^{1/2} \right\} \quad (14)$$

It can be seen from this expression that the solution (14) is non-real for $4\alpha/\sigma^2 > 1$, and is stable only for $x = 1/2$ (a racemate). Exceeding the critical noise level, defined by condition

$$\sigma_{\text{crit}}^2 = 4\alpha \quad (15)$$

the solution $x = 1/2$ becomes unstable and the system occupies a state with either $x = x_1$ or $x = x_2$. For $\sigma^2 \gg 4\alpha$ the values $x = 1$ or $x = 0$ represent the stationary solution. This means that a sufficiently intensive noise can transform an originally racemic state into a homochiralic one, i.e. a state with only L- or D-chiralic macromolecules. And this is exactly what we intended to prove.

Conclusion

It was demonstrated that the transformation of racemic compounds of L- and D-chiralic macromolecules to a homochiralic state in prebiotic era could have been due to a random influence of the medium, i.e. noise. This assumption is supported by the fact of the real existence in the biosphere of one class of macromolecules with pure L-chirality (aminoacids) and another one with pure D-chirality (saccharides). If just one deterministic factor, e.g. β -radiation, was responsible for the generation of homochirality, then it would be logical to expect only one pure chirality in the biosphere, i.e. either L- or D-types, which is not the case.

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