

LIFE AND CHIRALITY BEYOND THE EARTH

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Abstract. An attempt is made to show that the phenomenon of chirality – of which optical activity is but one consequence – is by no means restricted to life on Earth, but is common throughout the universe. Several independent sources have been investigated including: statistical fluctuations; stereoselective physical factors; and energetic differences between enantiomeric molecules. It is emphasized that a search for chirality as an indicator for life elsewhere in space provides an excellent tool for the fascinating question of exobiology. Still one must be aware of the limitations of the experimental methods and their interpretations.

1. Introduction

There is general agreement among scientists that chirality is a characteristic feature of living matter. The term 'chirality' is used here in the original sense of Van't Hoff: it describes the situation much better and more precisely than any other term such as 'optical activity', which is only one out of many consequences of the chiral structure of the molecules in question. Although a racemic mixture is also a chiral system because it comprises compounds of varying handedness, the term chirality is often an implicit reference to the fact that in nature chiral compounds of only one handedness prevail. If the statement of the first sentence were correct in a reciprocal way – i.e. 'where there are chiral compounds of one sign prevailing there is biology' and on the other hand 'where there are only non-chiral or racemic compounds there is no biology' – a systematic search for optical activity would be the most straightforward approach for the detection of life outside our planet.

As this essay will attempt to show, the situation is much less lucid than appears at first glance. Chirality is indeed a prerequisite for a system to be called biological, although chirality can well exist independently of the biological cell. Therefore the whole problem of applying the analysis of chirality in the search for life in the universe is considerably complicated. We believe that the problem can be solved bearing in mind some important points which would eventually lead to an unambiguous interpretation of any future optical activity analyses of extraterrestrial samples.

2. Chirality Due to Abiogenic Causes

2.1. STATISTICAL FLUCTUATIONS (CHANCE NUCLEATION)

The simplest way to achieve an optically active compound without biological interaction is the precipitation of a chemical chiral substance from its pure supersaturated solution. Unfortunately this method is applicable not to all, but only to a few chemical systems including some tartrates, amino acids and their derivatives.

The following describes such an experiment easily performed in any laboratory and outlines its physical interpretation: Let us dissolve a racemic substance, e.g. DL-glutamic acid, in water up to a saturated solution and cool the clear solution down until it becomes supersaturated – according to its endothermic solution characteristics. After some time without any further manipulation, there appear a few crystals which can be separated from the mother liquor, washed, and checked for optical activity polarimetrically. Even under the cleanest conditions it appears that very frequently the first crystals exhibit a fairly strong optical activity; a ‘spontaneous generation’ of chirality (of one sign!) would have been demonstrated. However this experiment works only if: (1) the compound tends to form a racemic conglomerate, and (2) the rate of nucleation is slow compared to the rate of growth of the crystals, a condition very often met by organic compounds. With the aid of Figure 1 the interpretation of this typical experiment will be given:

c is the concentration of the compounds in the supersaturated condition after the solution has been cooled down to an arbitrarily chosen lower temperature at time t_0 . c_s is the concentration corresponding to saturation of the compound at the same lower temperature. At time t_1 a first nucleus of, say, D-glutamic acid appears at random, whence crystallization of the D-enantiomer proceeds rather quickly following an exponential function. At the later time t_2 almost all D has precipitated, while the solution remains supersaturated with respect to the L-enantiomer. At time t_3 a first nucleus

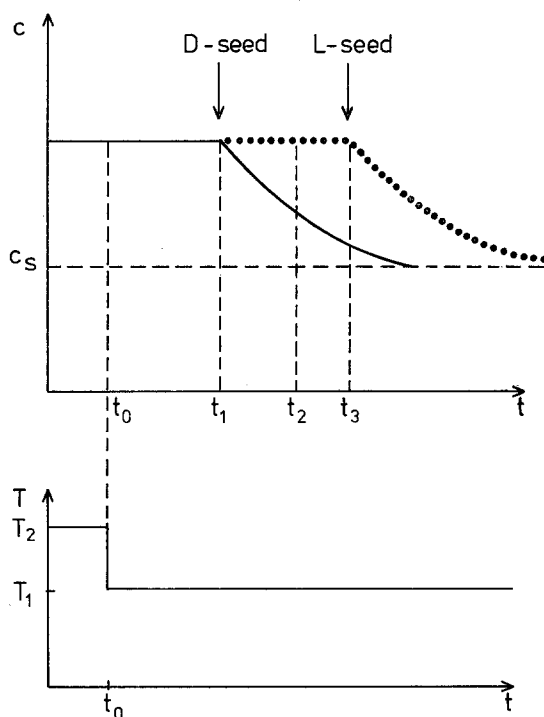


Fig. 1. Scheme of precipitation of a chiral substance from its supersaturated solution. Detailed explanation is given in the text.

of L-enantiomer is formed and the over-all thermodynamic equilibrium can be approached. At time t_{∞} , of course, the precipitate shows exactly the same composition as the initial solute – namely racemic; thermodynamic over-all equilibrium has been established.

This example is given here only as one of a great number of reactions leading to optically active compounds in a truly random fashion. Similar principles apply to chemical reactions, polymerizations, polycondensations, biochemical reactions, autocatalytic processes, and others. Basic models producing chiral compounds in a non-biogenic, random way have been proposed and partially experimentally tested by Prigogine (1961), Calvin (1969), Pincock *et al.* (1971), Seelig (1971a, b, 1972), Decker (1974), and Harrison (1974). There are mathematical calculations which lead to the conclusion that under specific conditions such as ‘hypercompetitive reactions’ or ‘autocatalytic kinetics’ the optically active products may well be thermodynamically favored over the racemic products.

2.2. PHYSICAL FACTORS CAUSING STEREOSELECTIVE SYNTHESSES OR DECOMPOSITIONS

A considerable amount of speculation as well as experimental results has been compiled demonstrating the capability of certain physical factors to influence organic syntheses or degradations in a stereoselective way, i.e. to enrich one enantiomer over the other in the product. The principal physical agents in question will be listed here:

(a) For a long time it has been expected that in a way similar to the production of circularly polarized light by optically active matter, circularly polarized light, in its turn, could induce optical activity in a prochiral or racemic system by stereoselective photochemical destruction. After many failures, experimental evidence for this hypothesis was finally produced by Kuhn and coworkers in 1929–30. During recent years many more facts have been reported in the literature supporting this stereoselective decomposition – and moreover – the synthesis of organic compounds by circularly polarized light. The mechanism of the interaction of light with chemicals is more interesting when considering the question of the chiral chemicals’ abundance in the universe, as circularly and elliptically polarized light seem to be abundant on Earth and on other planets including Mars, Venus, and Jupiter – three thoroughly investigated planets – (see e.g. Coffeen *et al.*, 1974). It should be emphasized that not only circularly polarized light as such exists in space but that this light emitted from the planets is predominantly polarized in the same sense!

Thus the earlier hypothesis of Byk (1904) and the later one of Mörtberg (1971) explaining the chiral biosphere as the result of the photochemical reaction of scattered sunlight with the terrestrial chemistry seems to have some justification. This reaction is depicted by the following scheme:

Overall: DL-A \rightarrow DL-B, to enrich the enantiomers, the
 reaction yield must be lower
 than 100%!

Specific: 50% D-A + 50% L-A \rightarrow 60% D-B + 40% L-B
 (D/L = 1) (D/L = 1.5)

It must be stressed, that this too, represents a model for a truly abiogenic creation of chirality.

(b) Another physical factor, whose stereoselective influence has been experimentally proved is the interaction of specific crystal surfaces with organic compounds. It is a case of a heterogeneous-type catalyzed chemical reaction. Although this principle had been discussed for a long time, it was not until very recently that unambiguous results were published (Bonner *et al.*, 1975) which show the stereospecific interaction of l- and d-quartz crystals with chiral compounds. The cited work of Bonner *et al.* does not really deal with chemical reactions but with stereoselective adsorption and desorption processes. Still unanswered remains the question, whether such chiral crystals as d- and l-quartz, or the corresponding kaolinite, montmorillonite, sodium chlorate, and other classical examples of this type were formed only after establishment of biological conditions on Earth!

(c) Various attractive hypotheses have been put forward postulating a stereospecific interaction of homogenous magnetic fields (such as exist on Earth, Jupiter, Mars and other planets), and/or electric fields with chemical compounds. Although the idea – going back to Curie (1894), and recently taken up in a very new and modified way by Noyes and Bonner (1974) – has a very sound theoretical basis it has thus far never been verified experimentally in spite of many efforts. Because of the abundance of homogeneous magnetic fields on the planets' surfaces this rather speculative model deserves to be kept in mind (see e.g. Neubauer, 1975).

(d) Shortly after the discovery of the parity violation of the weak interaction it was recognized by Vester (1957) that the chiral (i.e. moving in a helical path) β -particles emitted from the radioactive nuclei represent an analogy to the circularly polarized photons applied by Kuhn and coworkers in order to produce optically active compounds without biological interference. The analogy, however, is restricted mainly on two accounts:

(1) β -particles cannot directly interact with chemical bonds because of their high kinetic energy which must be attenuated by many successive collisions with the surrounding matter until they are thermalized. Thus, on their way through matter they lose their energy and to a great extent their polarization until they are able to react with the chiral molecules in question. It is not clear yet how much of the β -particles' polarization is lost on their way, how much of their polarization is transferred to circularly polarized γ -particles (Bremsstrahlung) and, further, to what extent the overall photochemical destruction is due to interaction with γ -rays.

(2) On the other hand there is a tremendous abundance of β -radiation of preferred chirality in nature. Obviously the inherent difficulty in achieving and explaining the origin of circularly polarized visible light in only one sense in the universe does not arise in the case of β -radiation, as long as we limit ourselves to the investigation of matter and not anti-matter, where positrons would be more abundant. Indeed if we consider the planet Earth as typical life-supporting system, there are great amounts of β -decaying radioactive nuclides in the crust, among them particularly K-40 which makes up the greatest part of natural radioactivity today. Unfortunately, here again

there exists very little positive evidence for the stereoselective interaction of β -particles with chiral or prochiral chemicals. Vester himself and coworkers (Ulbricht and Vester, 1962), who were first to draw attention to this idea, spent many years in the study of this subject, but did not succeed in producing any evidence supporting this hypothesis. So far the only positive results have been claimed by the group of Garay (Garay, 1968; Garay *et al.*, 1973), describing experiments with β -irradiation of D- and L-tyrosine in alkaline solution and with positron annihilation in solid D- and L-amino acids.

2.3. ENERGY DIFFERENCES BETWEEN ENANTIOMERIC MOLECULES

Starting from the same argument as above, namely the fact, that parity is not conserved in the weak interaction, Yamagata (1966) came to a rather unconventional hypothesis: he claimed that the familiar electromagnetic interaction itself – responsible for the chemical bond – would be parity-violated to a very small extent. Without going into details of this idea it may suffice at this point to state that Yamagata's postulate has been tested and largely confirmed by several theoretical and experimental indications (a recent work reviewing some results is given by Rein, 1974). An immediate result of this would be that D- and L-enantiomeric molecules should be distinguishable from each other not only by their vectorial but also by their scalar properties. This of course had to be demonstrated by a measurement of a difference of their energy content with all its consequences concerning other physico-chemical characteristics of the molecules. A straightforward chemical proof of this hypothesis has not been presented so far, due mainly to the fact that such an energy difference appears to be extremely small according to Rein (1974), namely in the neighbourhood of $10^{-10 \pm 2}$ eV! A few experiments indicate the possibility, however, that this figure could be greater by some orders of magnitude, although an explanation for this is lacking.

Lobashov *et al.* (1967) report a parity non-conservation of the μ -transition manifested in the polarization of the emitted μ 's of the order of -10^{-6} . In our laboratory we found that on the one hand solubilities of D- and L-enantiomers of sodium ammoniumtartrate and asparagine differ by a factor of about 10^{-4} to 10^{-6} from each other, while on the other hand rates of polycondensation of D- and L-lysine, alanine, and aminobutyric acid differ by a factor of about 10^{-6} . The details of these experiments are not given here, since they have been extensively published elsewhere (Thiemann and Darge, 1974; Thiemann, 1974). If these results could be reproduced and confirmed independently by other laboratories it would definitely upset the classical picture of enantiomer chemical systems being the exact mirror images of each other. This would lead to the attractive possibility that the chiral biosphere on our Earth would not be a random product of chance but the consequence of the physical laws responsible for the structure of matter itself. On the basis of this fundamental consideration, experiments are in progress to test this hypothesis by independent methods including: very sensitive spectroscopic techniques allowing the resolution of bands split by 10^{-6} eV or even smaller (microwave spectroscopy offers possibilities in this area), measurements of specific heats, investigations of irradiation *products* rather than of the decay of the *mother compounds*, etc.

3. Conclusion

From the above discussion it is clear that chirality as such – helical structures in chemical compounds as well as in physical phenomena – is a very common phenomenon throughout the universe. It follows that one must be very careful in interpreting any optical activity in extraterrestrial samples as indicative of living matter in the sample. This point has been worked out in more detail elsewhere (Thiemann, 1975). However, one should continue the search for optical activity as part of the quest for life in space, as long as the limitations of this approach are kept in mind. As far as we know from our limited experience on Earth, the biosphere itself is still the domain where optical activity is found in the greatest amount and purity. It appears that all other abiogenic processes have thus far been unable to produce this chirality to the same extent as biology has done. Either the over-all yield for generating this dissymmetry – say by circularly polarized light – was rather small, or the yield – say by random precipitation processes – was of statistically varying sign (changing from one experiment to the other) so at the end of a long series of independently undertaken experiments the over-all yield of optical activity was very small again. This seems to have been confirmed by the analyses of the organic contents of various chondrite meteorites and lunar samples for their D and L content (Ponnamperuma, 1974). The observed deviations of the ratio D to L from unity were so small and stochastic that a possible ‘biological’ origin of the samples could definitely not be supported. The situation would have been – and possibly will be – quite different if one were able to demonstrate consistently large deviations in the D/L ratio from unity (greater or smaller than 1) in future samples available from Mars or elsewhere.

References

- Bonner, W. A., Kavasmeneck, P. R., Martin, F. S., and Flores, J. J.: 1975, *Origins of Life* **6**, 367.
Byk, A.: 1904, *Z. Phys. Chemie* **49**, 641.
Calvin, M.: 1969, *Chemical Evolution*, Clarendon Press, Oxford.
Coffeen, D. L. et al.: 1974, *7th Plenary Meeting COSPAR, Sao Paulo, 16 June–1 July 1974*, (Proceedings in Press).
Curie, P.: 1894, *J. Phys.* **3**, 393.
Decker, P.: 1974, *J. Molec. Evol.* **4**, 49.
Garay, A. S.: 1968, *Nature* **219**, 338.
Garay, A. S., Keszthelyi, L., Demeter, J., and Hrasco, P.: 1973, *Chem. Phys. Letters* **23**, 549.
Harrison, L. C.: 1974, *J. Molec. Evol.* **4**, 99.
Kuhn, W. and Braun, E.: 1929, *Naturwiss.* **17**, 227.
Kuhn, W. and Knopf, E.: 1930, *Naturwiss.* **18**, 183.
Lobashov, V. M., Nazarenko, V. A., Saenko, L. F., Smotriskii, L. M., and Kharkwitsch, O. J.: 1967, *Phys. Letters* **25B**, 104.
Mörtberg, L.: 1971, *Nature* **232**, 105.
Neubauer, F. M.: 1975, *Lecture at Frühjahrstagung der Deutschen Meteorol. Gesellschaft und Arbeitsgemeinschaft Extraterrestrische Physik*, 3–7 March, 1975, Berlin.
Noyes, W. P. and Bonner, W. A.: 1974, in *Proc. Int. Symp. on Generation and Amplification of Asymmetry in Chemical Systems*, Report JÜL-CONF 13, KFA Jülich.
Pincock, R. E., Perkins, R. R., Ma, A. S., and Wilson, K. R.: 1971, *Science* **174**, 1018.
Ponnamperuma, C.: 1974, in *Proc. Int. Symp. on Generation and Amplification of Asymmetry in Chemical Systems*, Report JÜL-CONF 13, KFA Jülich.

- Prigogine, J.: 1961, in A. Marvis (ed.), *Theoretical Physics and Biology*, North Holland Publ. Co., Amsterdam.
- Rein, D.: 1974, *J. Molec. Evol.* **4**, 15, (with further references!).
- Seelig, F. F.: 1971, *J. Theor. Biol.* **31**, 355.
- Seelig, F. F.: 1971, *J. Theor. Biol.* **32**, 93.
- Seelig, F. F.: 1972, *J. Theor. Biol.* **34**, 197.
- Thiemann, W.: 1974, *J. Molec. Evol.* **4**, 85.
- Thiemann, W.: 1975, in *Life Sciences and Space Research XIII*, Akademie Verlag, Berlin, pp. 64.
- Thiemann, W. and Darge, W.: 1974, *Origins of Life* **5**, 263.
- Ulbricht, T. L. V. and Vester, F.: 1962, *Tetrahedron* **18**, 629.
- Vester, F.: 1957, *Seminar at Yale University*, 7 February, 1957.
- Yamagata, Y.: 1966, *J. Theor. Biol.* **11**, 495.