Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron: *Asymmetry* 15 (2004) 3171–3175
Tetrahedron: *Asymmetry*

# Symmetry breaking: an epistemological note

Martín Ávalos, Reyes Babiano, Pedro Cintas,* José L. Jiménez and Juan C. Palacios

*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Extremadura, E-06071 Badajoz, Spain*

Received 16 July 2004; accepted 23 August 2004
Available online 2 October 2004

Dedicated to Laurence D. Barron on the occasion of his 60th birthday

**Abstract**—In a record time the terms symmetry breaking and chiral symmetry breaking have gained a wide acceptance within the stereochemistry community. There has been a certain misuse of such terms as they are simply replacing well-established and unambiguous terms of the stereochemical glossary. Symmetry breaking is a useful and multifaceted concept that now pervades both physical and life sciences. This contribution is intended for tutorial purposes and for alerting scientists to pros and cons of chiral symmetry breaking with respect to previous nomenclature and more appropriate surrogates.

## 1. Introduction

Since the origins of optical activity and subsequently of handedness at the molecular level, stereochemistry and nomenclature have been invariably interlocked. A series of major treatises in the field include useful glossaries and IUPAC recommendations on stereochemistry are regularly published,[1,2] in the search for unambiguous interpretations and looking for universal criteria applicable to a wide spectrum of disciplines. Concepts such as chirality and asymmetry now influence fields ranging from nuclear physics to psychology. This paper addresses one of such appealing and, equally controversial, concepts. In the last decade, the term *symmetry breaking* (or alternatively *chiral symmetry breaking*) has become almost omnipresent in the vocabulary of asymmetric synthesis and catalysis. It may be astonishing to see that we are using that concept to simply denote examples of chiral discrimination or spontaneous resolutions, for which there are already precise definitions. What is indeed confusing is the fact that numerous chemists are invariably linking symmetry breaking with the (spontaneous) appearance of chiral patterns. Physicists, who first coined the term, and crystallographers among other scientists, have given it a broader and insightful view that stresses the importance of symmetry arguments in science.[3]

Our contribution is not intended to discourage the use of symmetry breaking; nevertheless the discussion helps set useful guidelines for a better understanding. Practitioners of asymmetric syntheses will have further elements to assess whether they are using a proper concept or only a smarter adornment.

## 2. Symmetry and physical laws

The intuitive essence of symmetry is the regular recurrence of certain patterns in an object or molecular structure. Symmetry appears to be a ubiquitous attribute of both the universe and nature. An in-depth analysis of symmetry also accounts for physical and molecular properties of matter.[3,4]

By the end of the 19th century the French physicist Pierre Curie was able to formulate a principle to define the symmetry (and its variations) of different physical phenomena.[5] Curie wrote: ‘When certain causes produce certain effects, the elements of symmetry of the causes must be found in the effects produced. When certain effects reveal a certain *dissymmetry*[6] this dissymmetry must be found in the causes that generated them. The opposite is not necessarily true, i.e., the effects produced may be more symmetrical that the causes that produced them’.

Broken symmetries, often viewed as reductions of symmetry,[7] are not so uncommon as one might anticipate.

---

* Corresponding author. Tel.: +34 924 289380; fax: +34 924 271149; e-mail: pecintas@unex.es

0957-4166/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2004.08.021

Several facts and analogies illustrate nicely this phenomenon. Symmetry breaking is what happens in cases of fluctuating asymmetry. The system is essentially symmetric but, occasionally, happens to have lost its symmetry. The problem is best illustrated by the celebrated allegory of Buridan's ass.[8] The French Aristotelian philosopher wondered what would happen to an ass placed exactly midway between two identical piles of hay.[9] Assuming that both piles are identical in every respect the ass would have no good reason to choose one of them and, as a consequence, the ass would die of starvation. The situation is entirely symmetric, but it is also unstable and any tiny external influence will move the ass slightly closer to one pile of hay than the other. The symmetry is broken and the ass will eat the pile that is that little bit closer. However, in another experiment, the ass could equally have approached to the other side. Buridan concluded that, in discerning both a symmetry of information and a symmetry of preference about two items, the ass must choose at random.

Consider, for instance, an atom in a liquid, which is equally likely to move in any direction in space, that is, there are no preferred coordinate axes. However, when the liquid is frozen and a crystal forms, the latter has distinguished axes. All directions in space are equally possible as crystal axes, but on freezing some distinguished axes will always appear. Thus, the symmetry between the all possible directions in space has been lost or spontaneously broken. Similarly, if one distorts (elongates or squashes) a sphere along one of its diameters, the isotropic character is also lost as gravitational effects may distinguish between vertical and horizontal directions. A third example is provided by an ordinary magnet. In the basic equations that describe the behavior of a lump of iron, any direction is equivalent to any other, but when iron becomes a magnet there will be some definite north-seeking pole.

An in-depth understanding of Curie's principle may be a difficult task, nevertheless. Physical systems may be dependent on parameters such as time, temperature, an external field as well as any other geometrical or chemical variable. When this parameter crosses a critical threshold, the system may then evolve into a nonsymmetrical configuration caused by a nonsymmetrical fluctuation. In short, spontaneous symmetry breaking implies that even if the fundamental equations that describe the laws of nature have a symmetry, the solutions of the equations may lack that symmetry.[10] Here, the term *spontaneous* breaking also implies that both the cause and its effect have the same symmetry. Spontaneous symmetry breaking is possible when a physical system or problem of a given symmetry possesses several degenerate configurations or solutions, all having the same although lower symmetry than that of the initial system.[11] Spontaneous symmetry breaking cannot satisfactorily be rationalized with the restricted formulation of Curie; it requires a more general approach that was developed by the Russian physicist and Nobelist Landau in the late 1930s.[12] Landau recognized that numerous phase transitions and order–disorder transitions are actually symmetry breaking phenomena. Thus, taking temperature as variable, there is usually reduction in symmetry on cooling such as in a smectic phase-crystal transition where the directions of the crystal axes impose a lower symmetry. In ferromagnetism, the ground state of an iron crystal is not invariant under spatial rotation as it distinguishes the specific direction of magnetization. When the temperature is raised above the Curie point, the magnetization disappears and the rotational symmetry becomes manifest. In other words, the symmetry is spontaneously broken in the low-temperature phase. There are exceptions to the preceding rule, which do not contradict thermodynamics, nevertheless. These include a nematic–smectic A phase transition or the case of Bose condensates, namely an ordered state in which many particles share the same quantum wave function (Einstein–Bose statistics). In helium this transition leads to superfluidity. Sometimes the association of symmetry breaking with an increase in order should be considered at local level, inclusion compounds providing a relevant example. The highest symmetries are usually found in systems that require the host molecules to be completely ordered, which are accompanied by some form of guest disorder. As a general rule, the more ideal the host, the more disorderly the guest. In these cases the symmetry breaking, observed in solid-state phase transitions as the temperature is lowered, directly corresponds to an entropy decrease.[13]

Crystals are without doubt plausible scenarios where local deformations as well as the presence of additives or impurities may lead to symmetry reductions,[7,14] which are detected in the form of optical anomalies. These have been attributed to nonequilibrium structures resulting from kinetically controlled crystal growth and occur when a crystal's symmetry is lower than its apparent structural symmetry as inferred from experimental techniques such as X-ray diffraction.[15] Symmetry breaking may yet have global consequences on the crystalline structure as in the case of polymorphic transitions, in which the space-group symmetry of the lower symmetry is a subgroup of that of the higher symmetry phase. A salient example is provided by the low-temperature polymorph of quartz (trigonal with space-group symmetry $P3_12$) and the high-temperature hexagonal polymorph (space-group symmetry $P6_222$). This transition could certainly be called symmetry breaking transition, although polymorphic changes are rarely denoted in this way. In fact, IUPAC disapproves of such a term.[16]

## 3. Symmetry breaking and asymmetry

As seen before, a preliminary difficulty with the term symmetry breaking is that it is not synonymous with *asymmetry* (at least in the molecular sense perceived by most chemists). This reflects the semantic puzzle often encountered in some stereochemical terms, that is, the universe of discourse determines the meaning or connotation of the wording, and therefore the spareness of a definition can engender a degree of fuzziness and variable interpretations, which are undesirable attributes in science.[17,18]

However, the relationship between symmetry and *dissymmetry* became evident at the onset.[5] The existence of optical rotation is only possible for substances whose molecules belong to chiral point groups. Like a pseudoscalar property, optical activity is invariant under a proper symmetry operation (rotation) but changes sign (that is, one enantiomorph is converted into another) under an improper symmetry operation (reflection). Curie himself showed, for instance, that a magnetic field does not break mirror-reflection symmetry, thereby explaining why asymmetric syntheses under magnetic fields previously performed by Pasteur were unsuccessful. Curie instead suggested collinear electric and magnetic fields.[19]

Likewise, symmetry properties dictate when a molecule will have a permanent dipole moment, which excludes $C_{nh}$ and dihedral ($D$) point groups, irrespective of the chiral content. Both piezoelectricity and pyroelectricity (generation of static electricity by mechanical action or heat, respectively) require that the crystals be noncentrosymmetric, which may be fulfilled by chiral substances or achiral ones crystallizing in chiral space groups.[20] Noncentrosymmetric crystals (either as enantiopure samples or conglomerates) are equally required for second-harmonic generation, that is, the incident photons are converted into a second beam with a frequency twice higher when light passes through a crystal.[21] This is indeed a hot topic and there is a fierce competition among scientists to create materials that show second-harmonic generation. Since the presence of noncentrosymmetry is the most stringent requirement for that phenomenon, the effect can also be exploited in chiral surfaces, interfaces, and thin films such as Langmuir–Blodgett films of chiral molecules.[22]

A comprehension of other properties requires going into the problem at a submolecular level, in which the concepts of asymmetry or symmetry breaking have well-established mathematical definitions, but the concept of chirality is certainly elusive. Physicists have long held a theory for superconductivity, dating back to the late 1950s, which requires materials with mirror symmetry. Very recently, it has been demonstrated that such a symmetry is no longer required. Thus, $CePt_3Si$ is a novel fermion superconductor at $T_c \sim 0.75\,K$.[23] The noncentrosymmetric structure lacks space inversion symmetry, which suggests an intriguing consequence. If the overall quantum state must be antisymmetric, both the spatial and spin parts of the wave function cannot simply be symmetric or antisymmetric. There must be a mixture of spin-singlet and spin-triplet states.[24]

When macroscopic phenomena, such as crystallization, are considered, things appear to be somewhat simpler. It is a certain truism to state that the spontaneous crystallization of a stereoisomer is a case of symmetry breaking. Crystallization itself is the phenomenon responsible of symmetry breaking, no matter whether the substance is chiral. That is, the system under consideration corresponds to a liquid–solid transition. In the condensation of a crystal from a collection of atoms, the spherical symmetry of each atom simply tells one that the crystal may be formed equally well with its axis pointing in any direction, although the experiment has no features that reflect a preference for a crystal structure. On vindicating repeatedly asymmetric crystallization as a case of symmetry breaking, we have thus abandoned the well-known terms of *asymmetric transformation of the first kind* and *asymmetric transformation of the second kind*, which have proven to be particularly useful in stereochemistry.[25] In the former, transformation of a mixture of stereoisomers into a single stereoisomer occurs by an equilibrium process without separation. In the case of enantiomers, the enrichment requires an asymmetric influence (either a chiral nonracemic solvent or an inherently chiral field). Two or more equilibrating chiral stereoisomers may eventually give rise to an crystallization-induced asymmetric separation, which represents a case of an asymmetric transformation of the second kind.

In our modern language, the Curie principle tells us that whenever chirality is observed in an object or structure, there must be a chiral component or influence in its precursors or causes. However, the contrary is not necessarily true because the effects of a chiral system with a nonchiral object do not inevitably reduce the symmetry of the nonchiral object. Numerous naturally-occurring organisms have surface structures (e.g., calcium carbonate shells) displaying macroscopic asymmetry.[26] The observed hillocks of calcite crystals have no mirror symmetry, which, according to the symmetry principle, suggests that there must be an asymmetric cause behind that effect. In biomineralization, the underlying asymmetry is provided by biomolecules that transmit a chiral morphology during crystal nucleation.[27] In spontaneous resolutions of conglomerates or phase transitions leading to chiral phases such as those observed in liquid crystals, the source of asymmetry may be uncertain, although it is, like Buridan's ass, stochastic to a large extent. Perhaps, the natural preference for L-amino acids (as well as D-sugars) remains one of the best examples of deviations from a perfect left–right symmetry. Whether left- or right-handedness was adopted was probably a matter of chance, but once a particular handedness was established, it maintained itself. This could imply that the chances should be equal of finding a terrestrial enantiomorph or its mirror image in extraterrestrial life forms.

These phenomena producing chiral objects or systems from achiral or racemic precursors are indeed cases of symmetry breaking or, much more accurately, of *mirror-symmetry breaking*. It should be emphasized that, from a conceptual viewpoint, such a breaking could also occur when any reaction of achiral materials would give rise to a chiral racemic mixture, that is, a molecular conglomerate.[28] These processes may be called cases of *chiral symmetry breaking* as recorded frequently in the literature, although that term also introduces a series of semantic and ambiguous interpretations. First, as remarked recently by Walba in an outstanding article on ferroelectric liquid crystals,[29] in physics the term chiral symmetry is not synonymous with left–right asymmetry, but equivalent to bilaterality and consequently, an object or system with *chiral symmetry is achiral*. Another linguistic contradiction appears when the word symmetry (rather than asymmetry) is used by life sciences. In biology symmetry is almost entirely used to mean bilateral symmetry or mirror symmetry, where one half of an object is the mirror reflection of the other half. Still in biology, and especially in psychology, it is convenient to distinguish between vertical (easily recognizable by our human perception) and horizontal bilateral symmetries.[30] Accordingly, the way in which the different scientific branches have adopted the term symmetry breaking is indeed a polysemous way, thus preventing immediate comparisons. How could we denote the (spontaneous) appearance of chirality?

To reconcile chemistry and physics (since in the latter chiral symmetry denotes congruent systems), Walba reasonably suggests *reflection symmetry breaking*[29] because the lack of reflection operations (alternating improper axes, reflection planes, and inversion centers) are associated with chiral molecules. The term is also equivalent to *mirror-symmetry breaking* or *space-inversion symmetry breaking* as commonly used in physics. Chemists could also understand without major conflict the alternative term of *achiral symmetry breaking* (fairly correct from a etymological point of view), although many scientists with a background in molecular chirality will certainly inquire whether they have heard correctly.[31] Strictly speaking, the only term that easily relates symmetry breaking and stereochemistry should surely be *desymmetrization*.[32] Here, in most cases from a formal viewpoint, removal of symmetry elements, molecular distortions, or substitutions on a symmetrical lattice framework can lead to figures or molecules with a reduced symmetry. Desymmetrization of *meso* compounds,[33] a well-known synthetic strategy or reactions at prochiral centers constitute, in principle, ways to symmetry reduction. Once again, symmetry breaking is not generally used in this context either. Such processes are not spontaneous in nature, nor do they constitute phase transitions.

## 4. Conclusions

Symmetry breaking is a rich, multifaceted concept that permeates numerous branches of knowledge. It provides a useful description of subatomic and molecular phenomena that are associated to phase transitions and order–disorder transitions. *Mirror-symmetry breaking* or *reflection symmetry breaking* are conceptually more appropriate and unambiguous than *chiral symmetry breaking* to denote the spontaneous appearance of chiral domains. Special caution should be paid to cases in which there are already a preexisting asymmetric state or nonracemic precursors such as in chiral amplification as well as in asymmetric synthesis and catalysis.[34]

## Acknowledgements

We express our appreciation to the Ministry of Science and Technology (Grants BQU2002-00015 and BQU2003-05946) for financial support.

## References

1. Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; pp 1191–1210.
2. IUPAC Recommendations on Stereochemistry: Moss, G. P. *Pure Appl. Chem.* **1996**, *68*, pp 2193–2222.
3. For a tutorial article emphasizing symmetry arguments in chemistry: Dunitz, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 14260–14266.
4. (a) Heilbronner, E.; Dunitz, J. D. *Reflections on Symmetry*; VCH: New York, 1993; (b) Hargittai, I.; Hargittai, M. *Symmetry through the Eyes of a Chemist*; VCH: New York, 1987; (c) Donaldson, J. D.; Ross, S. D. *Symmetry and Stereochemistry*; Wiley: New York, 1972; (d) Orchin, M.; Jaffé, H. H. *Symmetry Orbitals and Spectra*; Wiley-Interscience: New York, 1971.
5. (a) Curie, P. *J. Phys. Theor. Appl. (Paris)* **1894**, *3*, 393–415; (b) Curie, P. *Oeuvres*; Gauthier-Villars: Paris, 1908 (Reprinted: Archives Contemporaines: Paris, 1984).
6. Dissymmetry is a now-obsolete term introduced by Pasteur, Curie, and other pioneers in the 19th century. In the older literature it is used as a synonym for chirality. Note, however, that chirality cannot be equated with asymmetry (namely, the complete absence of symmetry; Ref. 1, p 72). In his classic textbook on stereochemistry, Mislow noted that molecular arrangements without reflection symmetry are called dissymmetric or chiral. No dissymmetric conformation can have a $\sigma$ plane. If a $C_n$ ($n > 1$) is also absent, the molecule lacks all symmetry elements and is therefore called asymmetric (point group $C_1$): Mislow, K. *Introduction to Stereochemistry*; Benjamin/Cummings: Reading, MA, 1965; p 25.
7. The existence of symmetry breaking often implies a reduction of symmetry and, thus most of the symmetry-breaking transitions undergone by crystals and other systems correspond to symmetry reductions. The term *reduction*, however, also points to a certain quantification with respect to the original situation. In group theory this could be accomplished by analyzing the existing symmetry elements that function as symmetry operators. Thus, molecules in point group $C_1$ have the lowest degree of symmetry (identity is the only symmetry element). Yet another potential problem is the possibility of an averaged symmetry, due to rapid interconversion of the contributing conformers on a time scale. Cyclohexane (chair form) has a $D_{3d}$ symmetry, but experimentally at room temperature it simulates the higher symmetry $D_{6h}$ characteristic of a planar arrangement (e.g., benzene).
8. (a) Altmann, S. L. *Icons and Symmetries*; Clarendon: Oxford, 1992; p 28; (b) Van Fraassen, B. C. *Laws and Symmetry*; Clarendon: Oxford, 1989; p 240.
9. Jean Buridan (1300–1358) was Rector of the University of Paris (the Sorbonne). Curiously the animal mentioned in Buridan's commentary on Aristotle's *De Caelo* (On the Heavens) is actually a dog not an ass.
10. (a) We have learned that some fundamental physical laws may not be entirely symmetric. Parity or space inversion conservation is not a perfect symmetry of nature. In particle physics symmetry breaking is usually connected with the theory of supersymmetry, which relates fermions to bosons in an approach to incorporating gravity into a unified theory with strong and electroweak interactions Kane, G. *Supersymmetry: Unveiling the Ultimate Laws of Nature*; Perseus Books: New York, 2001; (b) For some recent essays: Wilczek, F. *Nature* **2004**, *428*, 261; (c) Witten, E. *Nature* **2004**, *429*, 507–508.
11. De Gennes, P. G. In *Symmetries and Broken Symmetries in Condensed Matter Physics*; Boccara, N., Ed.; IDSET: Paris, 1981; Chapter 1.

12. (a) Landau, L. D.; Lifschitz, E. M. *Statistical Physics*; Pergamon: London, 1959; Chapter 3; For a comprehensive yet non-mathematical treatment, see: (b) Sivardiere, J. *La Symetrie en Mathematiques, Physique et Chimie (Symmetry in Mathematics, Physics and Chemistry)*; Presses Universitaires: Grenoble, 1995; Chapter 43, pp 715–735.
13. Rutherford, J. S. *Cryst. Eng.* **2001**, *4*, 269–281.
14. Addadi, L.; Berkovitch-Yellin, Z.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. *Top. Stereochem.* **1986**, *16*, pp 1–85.
15. For an excellent survey: Kahr, B.; McBride, J. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1–26.
16. McNaught, A. D.; Wilkinson, A. *Compendium of Chemical Terminology. IUPAC Recommendations*, 2nd ed.; Blackwell: Oxford, 1997, See also: *Pure Appl. Chem.* **1994**, *66*, 591.
17. (a) Mislow, K. *Top. Stereochem.* **1999**, *22*, 1–82; (b) Mislow, K. *Chirality* **2002**, *14*, 126–134.
18. Rouvray, D. H. In *Concepts in Chemistry: A Contemporary Challenge*; Rouvray, D. H., Ed.; Wiley: New York, 1997, Chapter 1.
19. Collinear electric and magnetic fields do not generate molecular chirality either. Pierre Curie ignored the role of time reversal (*T*), characteristic of motion-dependent chirality. Time reversal of one of the enantiomorphous states (interconverted by space inversion *P*) combined with any proper rotation gives rise to a homomorph of the former. Pseudoscalar properties such as natural optical activity and hence chirality are only supported by a *T*-invariant enantiomorphism that is, *T* cannot undo the effect of space inversion (*P*): (a) Barron, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 5539–5542; (b) Barron, L. D.; Buckingham, A. D. *Acc. Chem. Res.* **2001**, *34*, 781–789.
20. Paul, I. C.; Curtin, D. Y. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987, Chapter 9.
21. (a) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley-Interscience: New York, 1984; (b) Ball, P. *Made to Measure. New Materials for the 21st Century*; Princeton University: Princeton, NJ, 1984; pp 51–52.
22. Verbiest, T.; Persoons, A. In *Materials-Chirality, Topics in Stereochemistry*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Wiley: New York, 2003; Vol. 24, pp 519–570, and references cited therein.
23. (a) Bauer, E.; Hilscher, G.; Michor, H.; Paul, C.; Scheidt, E. W.; Gribanov, A.; Seropegin, Yu.; Noël, H.; Sigrist, M.; Rogl, P. *Phys. Rev. Lett.* **2004**, *92*, 027003; For a commentary: (b) Saxena, S. S.; Monthoux, P. *Nature* **2004**, *427*, 799.
24. In magnetic superconductors such as metals or alloys, the state wave function can be separated into two parts, one depending only on the spatial coordinates and the other only on the spin coordinates. In crystals with space-inversion (parity) symmetry, the interchange of the spatial coordinates of the electrons gives rise to a state indistinguishable from the original. Therefore, the probability distribution of the electrons in the state wave function remains unaffected. A second interchange gives back the initial quantum state, with a phase factor of $+1$ or $-1$, that is, the spatial part must be either symmetric or antisymmetric. If the complete state has to be antisymmetric (electron states have momenta equal in magnitude, but opposite in direction), the spin part of the wave function must be antisymmetric (it must have the opposite symmetry under electron interchange). This implies a spin-singlet state, typical of metals such as aluminum. Conversely, an antisymmetric spatial wave function requires a symmetric spin wave function (corresponding to a spin-triplet state).
25. (a) See Ref. 1, p 1193; (b) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley: New York, 1981; p 370; (c) Hassan, N. A.; Bayer, E.; Jochims, J. C. *J. Chem. Soc.*, *Perkin Trans. 1* **1998**, pp 3747–3757.
26. In other words the observable pattern, which has in principle no relation with the intimate structure. In crystallography, the packing may present low symmetry as revealed by the asymmetry of the electron diffraction pattern, although the single crystals be highly symmetric. For an excellent discussion: De Rosa, C. In *Materials-Chirality, Topics in Stereochemistry*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Wiley: New York, 2003; Vol. 24, pp 71–155 (especially pp 109–121).
27. (a) Bouropoulos, N.; Weiner, S.; Addadi, L. *Chem. Eur. J.* **2001**, *7*, 1881–1888; (b) Orme, C. A.; Noy, A.; Wierzbicki, A.; McBride, M. T.; Grantham, M.; Teng, H. H.; Dove, P. M.; DeYoreo, J. J. *Nature* **2001**, *411*, 775–779.
28. Conglomerate refers to a mechanical mixture of two enantiomers forming a eutectic. The term is reserved for a mixture of macroscopic chiral domains although it is not only confined to crystals but also to two-dimensional conglomerates such as Langmuir films. For chiral morphologies of Langmuir monolayers see: Nandi, N.; Vollhardt, D. *Chem. Rev.* **2003**, *103*, 4033–4075. In stark contrast *true racemates* contain equal numbers of enantiomeric molecules within the unit cell, that is, they are composed of achiral domains containing chiral elements of opposite handedness forming an achiral system.
29. Walba, D. M. In *Materials-Chirality, Topics in Stereochemistry*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Wiley: New York, 2003; Vol. 24, pp 457–518.
30. McManus, C. *Right Hand, Left Hand. The Origins of Asymmetry in Brains, Bodies, Atoms and Cultures*; Harvard University: Cambridge, MA, 2002; Chapter 14.
31. Achiral symmetry breaking is also to be discouraged because supramolecular aggregates composed of chiral nonracemic molecules may display no chirality (achiral phases), such as in mesogenic structures; see for instance: Doren, H. H. v.; Smits, E.; Pestman, J. M.; Engberts, J. B. F. N.; Kellogg, R. M. **2000**, *29*, pp 183–199.
32. See Ref. 1, pp 88–91 and references cited therein.
33. (a) Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1096–1109; (b) Walsh, P. J.; Lurain, A. E.; Balsells, J. *Chem. Rev.* **2003**, *103*, 3297–3344.
34. Mikami, K.; Yamanaka, M. *Chem. Rev.* **2003**, *103*, 3369–3400.