

Dissymmetry and Asymmetry

A Hopeless Conflict in Chemical Literature

Chandan Saha and Suchandra Chakraborty



(left) Chandan Saha is an Assistant Professor in the Department of Clinical and Experimental Pharmacology, School of Tropical Medicine, Kolkata. He is engaged in teaching and research in synthetic chemistry.

(right) Suchandra Chakraborty is a Senior Research Fellow in the Department of Clinical and Experimental Pharmacology, School of Tropical Medicine, Kolkata. She is carrying out her research under the supervision of Chandan Saha.

In French science literature, the term dissymmetry appeared as early as in 1820, before Louis Pasteur. Pasteur, a French scientist, in his lecture ‘*Recherches sur la Dissymétrie Moléculaire des Produits Organiques Naturels*’ in 1860 used the term dissymmetric which was translated in English as asymmetric. A methodical study of his work reveals that the choice of the word dissymmetry is ideal even in the context of present-day science. Strictly speaking, there should be no conflict between the two terms dissymmetry and asymmetry.

1. Introduction

A careful study of the life history of Louis Pasteur (1822–1895), French chemist and biologist, founder of bacteriology and microbiology, reveals that he used words skillfully in his scientific writings and lectures. He used to convey his scientific ideas precisely and clearly and had outstanding proficiency in scientific communication.

Tartaric acid had been identified by ancient Romans as its monopotassium salt, tartar, which deposits from fermenting grape juice. Tartaric acid derived from tartar was one of the compounds examined by Jean-Baptiste Biot (1774–1862) for optical activity. He observed that it had a positive rotation. An isomer (according to Biot) of tartaric acid noticed in crude tartar, called paratartaric acid or racemic acid (*racemes*, Latin for a ‘bunch of grapes’), was also studied by Biot and found it to be optically inactive. The exact relationship between (+)-tartaric acid and racemic acid remained obscure at his time.

An excerpt of the English translation [1] of the French lecture *Recherches sur la Dissymétrie Moléculaire des Produits*

Keywords

Louis Pasteur, symmetry, dissymmetry, asymmetry, chirality.



Box 1. Excerpt from Louis Pasteur's 1860 Lecture

I must first place before you a very remarkable note by Mitscherlich which was communicated to the Académie des Sciences by Biot. It was as follows:-

“The double paratartrate and the double tartrate of soda and ammonia have the same chemical composition, the same crystalline form with the same angles, the same specific weight, the same double refraction, and consequently the same inclination in their optical axes. When dissolved in water their refraction is the same. But the dissolved tartrate deviates the plane of polarisation, while the paratartrate is indifferent, as has been found by M. Biot for the whole series of those two kinds of salts. Yet, adds Mitscherlich, “here the nature and number of the atoms, their arrangement and distances, are the same in the two substances compared.”

This note of Mitscherlich's attracted my attention forcibly at the time of its publication. The above note disturbed all my ideas. Did two substances exist which had been more fully studied and more carefully compared as regards their properties? But how, in the existing conditions of the science, could one conceive of two substances so closely alike without being identical? In short, Mitscherlich's note remained in my mind as a difficulty of the first order in our mode of regarding material substances. I thought at once that Mitscherlich was mistaken on one point. I hastened therefore to re-investigate the crystalline form of Mitscherlich's two salts. I found, as a matter of fact, that the tartrate was hemihedral, like all the other tartrates which I had previously studied, but, strange to say, the paratartrate was hemihedral also. Only, the hemihedral faces which in the tartrate were all turned the same way, were, in the paratartrate inclined sometimes to the right and sometimes to the left. In spite of the unexpected character of this result, I continued to follow up my idea. I carefully separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined their solutions separately in the polarising apparatus. I then saw with no less surprise than pleasure that the crystals hemihedral to the right deviated the plane of polarisation to the right, and that those hemihedral to the left deviated it to the left; and when I took an equal weight of each of the two kinds of crystals, the mixed solution was indifferent towards the light in consequence of the neutralisation of the two equal and opposite individual deviations.

Organiques Naturels by Louis Pasteur, in 1860, is given in *Box 1*.

From this lecture, today we recognize that Pasteur had achieved the first resolution of a racemic mixture, that is, paratartaric acid or racemic acid is actually (\pm) tartaric acid. In this connection, it is worth mentioning that Pasteur used the term Hemihedral. For the present purpose, hemihedrism may be described as the absence of a plane, centre, or alternating axis of symmetry in a crystal. In 1801, the phenomenon of hemihedrism of certain quartz crystals was observed by the French mineralogist Hauy



In 1821, Sir John Herschel, British astronomer, noted that all quartz crystals having the odd faces inclined in one direction (i.e., the crystals of one type of hemihedrism) rotate plane polarized light in one and the same direction, whereas the mirror-image crystals (i.e., the crystals of the other type of hemihedrism), whose odd faces are inclined in the opposite direction rotate plane polarized light in the opposite direction.

“But it cannot be a subject of doubt that there exists an arrangement of the atoms in ... order, having a non-superposable image.”

– *Louis Pasteur*

who recognized two varieties of quartz crystals related as object and incongruent mirror image. In 1821, Sir John Herschel, British astronomer, noted that all quartz crystals having the odd faces inclined in one direction (i.e., the crystals of one type of hemihedrism) rotate plane polarized light in one and the same direction, whereas the mirror-image crystals (i.e., the crystals of the other type of hemihedrism), whose odd faces are inclined in the opposite direction rotate plane polarized light in the opposite direction. Till then, the consequence of hemihedrism was the existence of an object and its incongruent mirror image. In addition, hemihedrism was somehow related with optical activity. Pasteur made several inferences (all correct) based on his experiment. Mainly, he had unambiguously ascertained the existence of molecular dissimilarity in the following form: “Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron, or disposed according to some particular ... grouping or other? We cannot answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in ... order, having a non-superposable image.”

A point to be noted is that in the year 1860, there was no idea about the tetrahedral tetravalency of carbon. In the concluding part of his 1860 lecture, Pasteur said: “Il y a dissymétrie moléculaire des produits organiques naturels. La vie est fonction de la dissymétrie de l’Univers. Seuls les produits nés sous l’influence de la vie sont dissymétriques, cela parce qu’à leur élaboration président des forces cosmiques qui sont elles-mêmes dissymétriques”.

Unfortunately, the title was translated into English as ‘Researches on the Molecular Asymmetry of Natural Organic Products’ and the above text as: “There are molecular asymmetry of natural organic products. Life is a function of the asymmetry of the Universe. The only products born under the influence of life are asymmetrical, this president because in their development of cosmic forces that are themselves asymmetrical.”

So the confusion and controversy arise from this translation.



- Whether dissymmetry and asymmetry are synonymous?
- Whether Pasteur used the word ‘dissymmetric’ cautiously?
- Whether Pasteur used the word dissymmetric just to indicate the meaning ‘not symmetric’, i.e., lack of symmetry?

It is worthwhile to mention that ‘asymmetry’ had been in use in French since 1691, but Pasteur ignored it in favour of ‘dissymmetry’. ‘Dissymmetric’ first appeared in the early 1820s (even before Pasteur was born) in French scientific literature, and was used in crystallography and other circumstances. Its meaning was ‘dissimilar or different in appearance or lack of symmetry’.

It is worthwhile to mention that ‘asymmetry’ had been in use in French since 1691, but Pasteur ignored it in favour of ‘dissymmetry’.

2. Superimposable and Non-superimposable Molecules

Later, developments in understanding molecular structures led to recognising that molecules that lack symmetry exhibit optical activity. In simple terms, we now know that only that substance whose molecular configuration is not superposable on its mirror image is optically active. Consequently, a compound with the mirror image molecular configuration is also optically active. This phenomenon is related to handedness and is called chirality (Greek *cheir*, for hand). A chiral molecule is defined as one whose molecular configuration is not superposable on its mirror image configuration. Optical activity as well as chirality are closely related to molecular symmetry.

There are several terms connecting molecular symmetry, optical activity and chirality. Ernest L Eliel [2] summarizes these relationships as in *Table 1*.

Table 1. Relationship between symmetry and optical activity.

Term	Alternating axis of symmetry	Simple axis of symmetry	Optical activity
Symmetric	Present	May or may not be present	Inactive
Dissymmetric	Absent	May or may not be present	Usually active
Asymmetric	Absent	Absent	Usually active



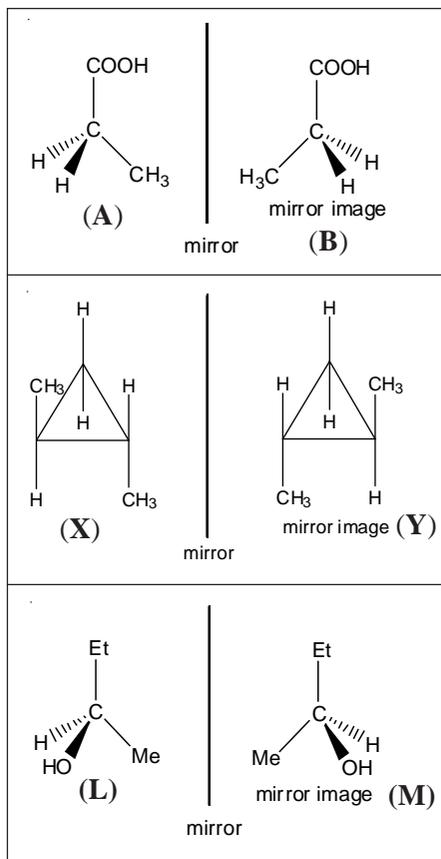


Figure 1 (top). Propionic acid.

Figure 2 (center). *trans*-1,2-dimethylcyclopropane.

Figure 3 (bottom). 2-butanol.

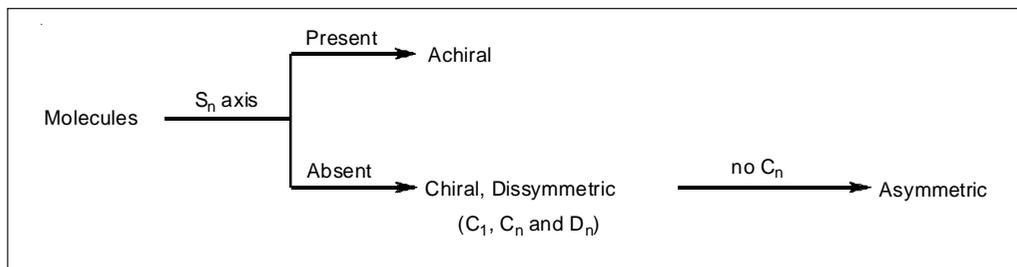
To explain the contents of *Table 1*, let us consider some simple examples. In the case of propionic acid, (*Figure 1*), the molecular configuration (A) contains a plane of symmetry which is the plane of the paper (equivalent to S_1), but there is no simple axis of symmetry. So propionic acid (A) is symmetric. If we take a close look at its mirror image configuration (B), we find that it is superposable by turning it around the C–COOH bond and thus it is optically inactive.

In the case of *trans*-1,2-dimethylcyclopropane (*Figure 2*), the molecular configuration (X) contains a two-fold simple axis of symmetry passing through C₃ and mid-point of C₁–C₂ bond, but there is no alternating axis of symmetry. So, *trans*-1,2-dimethylcyclopropane with the molecular configuration (X) is dissymmetric. On a closer scrutiny of its mirror image configuration (Y), we find that they are not superposable and thus are optically active.

In the case of 2-butanol (*Figure 3*), the molecular configuration (L) is devoid of any elements of symmetry (i.e., no S_n or C_n), except C_1 which is a trivial one.

So in accordance with *Table 1*, 2-butanol with the molecular configuration (L) can be described as either dissymmetric or asymmetric. From *Table 1*, it appears that all asymmetric molecules are dissymmetric, but the reverse is not true as dissymmetric *trans*-1,2-dimethylcyclopropane with the molecular configuration (X) possessing only two-fold simple axis of symmetry cannot be illustrated as asymmetric. Even in literature, 2-butanol with the molecular configuration (L) is always described solely as asymmetric. On a closer scrutiny of its mirror image configuration (M), we find that the two are not superposable and thus it is optically active. Again in *Table 1*, the term ‘usually active’ is rather confusing. First of all, it signifies that optical activity will be exhibited in a majority of the cases and at least a few compounds may be optically inactive or achiral. Therefore, the question is whether the absence of alternating axis of symmetry is not





a sufficient condition for a compound to show optical activity. As a result, *Table 1* needs further clarification.

Scheme 1.

This was expressed in a different form in the book by D Nasipuri [3] and is shown here in *Scheme 1*.

From this scheme, it appears that the absence of alternating axis of the symmetry is a sufficient condition for a compound to display optical activity. But, this is not in accordance with *Table 1*, which indicates that a molecule which does not contain an alternating axis of symmetry is usually active. Again, in *Scheme 1*, the statement ‘chiral, dissymmetric’ is used for a molecule which does not possess alternating axis of symmetry. From this, can we describe all chiral molecules as dissymmetric? In the same book, it is stated that: “The term chiral (whence chirality) is synonymous with dissymmetric (Eliel and Wheland 1962) although the former being getting wider currency”. But, the wider currency of chirality is not discussed. Regarding the term asymmetric, the book has the following statement, “The term asymmetric (or asymmetry) has a slightly different connotation in the sense that while an asymmetric molecule is a chiral molecule, it lacks C_n axis also; i.e., all symmetry elements are absent except for the trivial C_1 axis”. Thus, the confusion arises from the portions “The term chiral (whence chirality) is synonymous with dissymmetric” and “while an asymmetric molecule is a chiral molecule, it lacks C_n axis also”. Whence, it appears that all asymmetric molecules are dissymmetric but the reverse is not true as dissymmetric molecules may belong to the point group C_n ($n > 1$) or D_n . However, there is no such statement.



Figure 4. Lactic acid molecule.

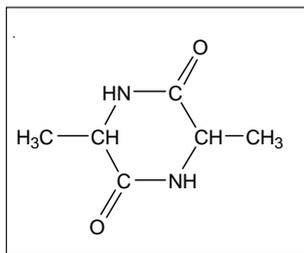
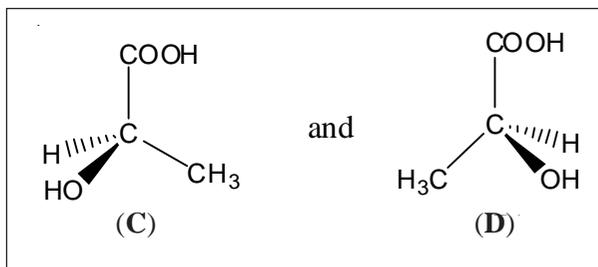
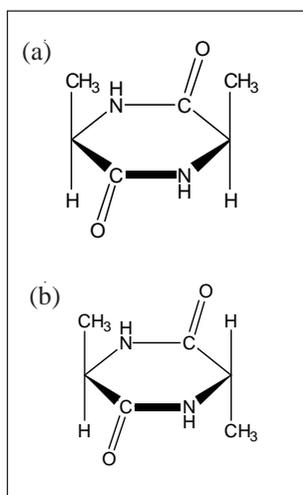


Figure 5. 3,6-dimethyl-piperazine-2,5-dione.

Figure 6.

(a) *cis*-3,6-dimethyl-piperazine-2,5-dione.

(b) *trans*-3,6-dimethyl-piperazine-2,5-dione.



Let us consider the following definitions in an edition of Ernest L Eliel's book [4] which gives a clearer picture.

Achiral: An entity, such as a molecule, is achiral if it is superposable with its mirror image.

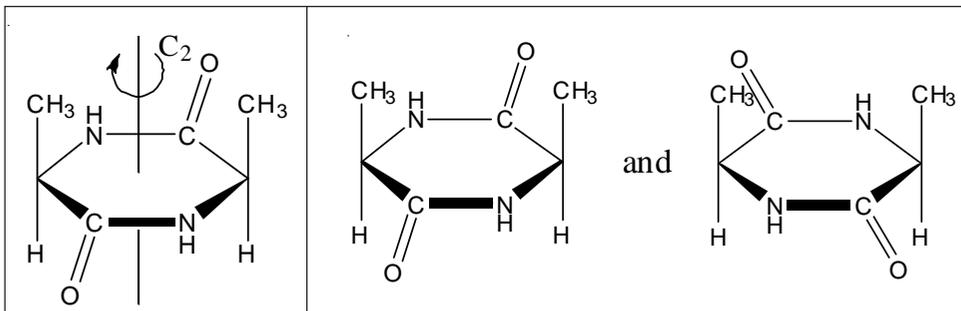
Chiral: Not superposable with its mirror image, as applied to molecules, conformations, as well as macroscopic objects, such as crystals. The term has been extended to samples of substances whose molecules are chiral, even if the macroscopic assembly of such molecules is racemic.

Dissymmetric: Obsolete synonym of chiral. Not equivalent to asymmetric, since dissymmetric or chiral entities may possess C_n axes ($n > 1$).

Asymmetric: Lacking all elements of symmetry (other than the identity E or C_1); belonging to the symmetry point group C_1 .

We study the following examples to clear almost all the previous confusions and contradictions. Consider the configuration (C) of lactic acid molecule (Figure 4). Obviously, this molecular configuration contains no elements of symmetry except the trivial C_1 . Thus, it is a molecule in the point group C_1 (contains neither S_n nor C_n , $n > 1$) and asymmetric. The molecule is chiral, as its mirror image configuration (D) is not superposable on (C). Therefore, lactic acid is resolvable into two enantiomeric forms, (C) and (D) (Figure 4).

Let us consider the case of 3,6-dimethyl-piperazine-2,5-dione (Figure 5). It can exist in *cis* and *trans* isomeric forms (Figure 6).



The *cis*-isomer contains a C_2 axis only, as shown in *Figure 7*, and is in the point group C_2 (has no S_n but contains C_n , $n = 2$) and thus is dissymmetric. Again the molecule is chiral. So, this compound is resolvable into two enantiomeric forms which are given in *Figure 8*.

On the other hand, the *trans*-isomer contains a centre of symmetry only, which is the centre of the ring as shown in *Figure 9*. Thus, the molecule is undoubtedly symmetric, hence achiral and is superposable on its mirror image and it is a molecule in the point group C_i .

Let us consider another interesting molecule 'twistane' shown in *Figure 10*. Twistane possesses three mutually perpendicular C_2 axes as shown in *Figure 11*. Therefore, it is a molecule in the point group D_2 and is dissymmetric. It is a chiral molecule and thus can exist in two enantiomeric forms.

From the above discussions, we can clear our concepts regarding dissymmetry. However, from the latest [4] definition of 'dissymmetric', it is apparent that only the phrase 'may possess C_n axes

Figure 7 (left).

3,6-dimethyl-piperazine-2,5-dione.

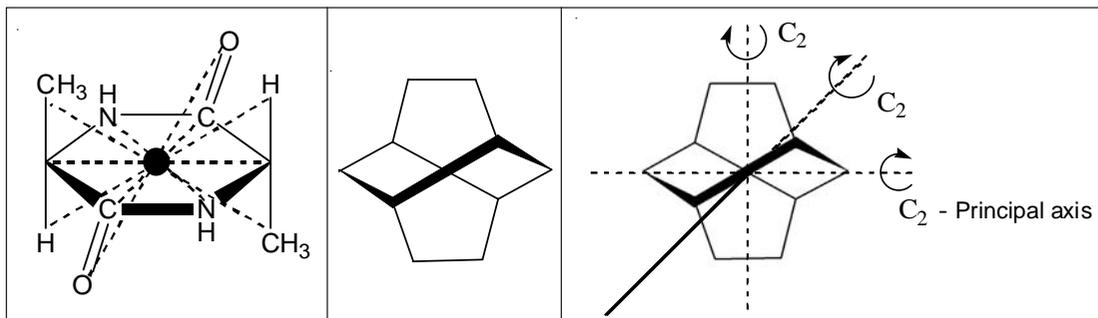
Figure 8 (right).

Enantiomeric forms of *cis*-3,6-dimethyl-piperazine-2,5-dione.

Figure 9 (left). *trans*-3,6-dimethyl-piperazine-2,5-dione.

Figure 10 (center). Twistane.

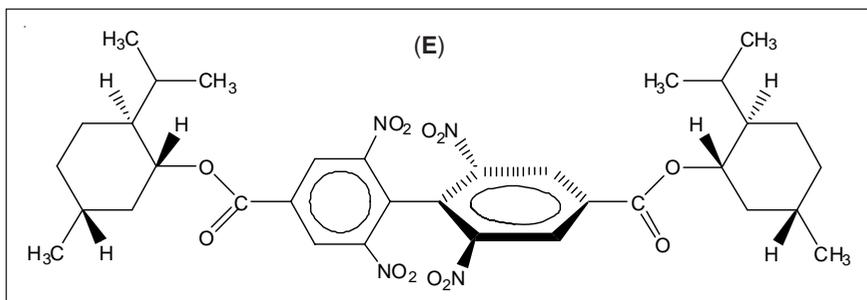
Figure 11 (right). Enantiomeric form of twistane.

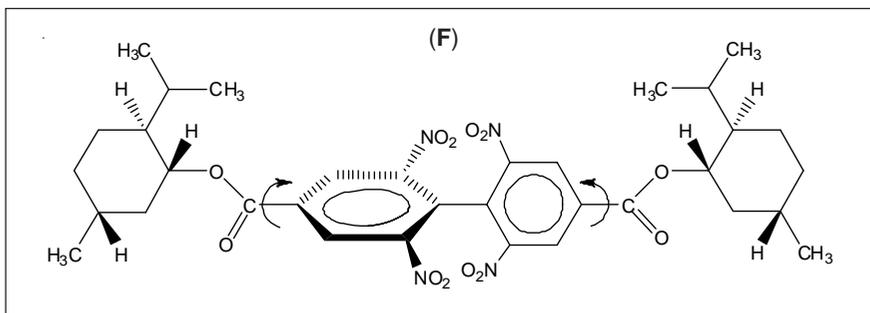


($n > 1$), is somewhat confusing. Obviously, the words ‘may possess’ mean both ‘may possess’ and ‘may not possess’. From the examples discussed so far, we are forced to conclude that a better definition of dissymmetric will be ‘obsolete synonym of chiral, not equivalent to asymmetric, since dissymmetric chiral entities must possess C_n axes ($n > 1$)’, i.e., the word ‘must’ should be introduced in place of ‘may’. In addition, ‘dissymmetric or chiral entities’ in the definition should be replaced by ‘dissymmetric chiral entities’, i.e., dissymmetric should be the adjective of chirality to avoid any sort of confusion and contradiction. From the given examples, it appears that both dissymmetric and asymmetric molecules are chiral. Thus both the terms, dissymmetry and asymmetry, should be used as adjectives of chiral; then only, the origin of chirality will be clear. In this context, it is worth considering the examples of dissymmetric chiral molecules, *trans*-1,2-dimethylcyclopropane (**X** or **Y** of *Figure 2*), *cis*-3,6-dimethyl-piperazine-2,5-dione (*Figure 7*), twistane (*Figure 10*) and the asymmetric chiral molecules, 2-butanol (**L** or **M** of *Figure 3*) and lactic acid (*Figure 4*).

Although it is generally true that asymmetric or dissymmetric compounds are optically active, the compound in *Figure 12* is inactive though it is devoid of any symmetry elements except C_1 . Here the presence of two phenyl rings on perpendicular planes leads to the absence of any symmetry element except C_1 . But the lack of optical activity of this compound is attributed to the fact that the molecule (**E**) and mirror image (**F**) (*Figure 13*, mirror image is drawn by placing the mirror vertically on the right side) though not superposable, can be made superposable by rotation

Figure 12. (-)menthyl(+)
menthyl-2,2',6,6'-tetranitro-
biphenyl-4,4'-dicarboxylate.





around the bonds linking the carboxylate groups to the ring (as shown in the *Figure 13*) through 90° .

This clarifies the term ‘usually active’ in *Table 1*. As a result, a new term is introduced ‘averaged symmetry’ [3], which means “because of a rapid interconversion of structures on a time-scale that is appreciably faster than that of the technique designed to determine the symmetry of any of its structures, the molecule indirectly possesses higher symmetry than the symmetry present in any of its contributing structures”.

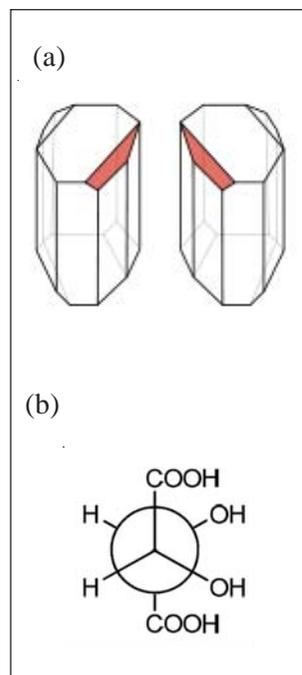
3. Conclusion

Dissymmetry and asymmetry are two different molecular properties with respect to symmetry and both are indicative of the chirality of the molecule. The source of the confusion was the improper translation of Louis Pasteur’s lecture (1860) from French to English. We suggest appropriate usage of the terms ‘dissymmetric chiral molecules’ and ‘asymmetric chiral molecules’. We find that Pasteur used the term ‘dissymmetry’ of the molecules based on his studies of the symmetry property of quartz crystals and the crystals of sodium-ammonium tartarate in 1848. Pasteur was well aware of the fact that the crystals of sodium-ammonium tartarate contain a three-fold axis of symmetry (principal axis) and three two-fold axes, i.e., the crystal is dissymmetric having D_3 point group (*Figure 14*). Pasteur had deliberately chosen the word ‘dissymmetry’ with full knowledge of its meaning, although the French science dictionary contains both the words ‘asymmetry’ and ‘dissymmetry’.

Figure 13. Mirror image of (E) shown in *Figure 12*.

Figure 14.

- (a) Crystals of sodium-ammonium tartarate.
(b) Active tartaric acid.



If we consider the optically active tartaric acid, we recognize that the preferred conformation (*Figure 14*) possesses a C_2 axis passing horizontally through the mid-point of C_2-C_3 bond, i.e., the molecule is a dissymmetric chiral entity. Thus, the choice of the word ‘dissymmetry’ by Louis Pasteur was accurate.

Suggested Reading

- [1] *Researches on the Molecular Asymmetry of Natural Organic Products*, Alembic Club Reprints, No.14.
- [2] Ernest L Eliel, *Stereochemistry of Carbon Compounds*, Tata McGraw-Hill, first edition, 1975, 18th Reprint 1993.
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Address for Correspondence

Chandan Saha¹ and
Suchandra Chakraborty²
Department. of Clinical and
Experimental Pharmacology
School of Tropical Medicine
Kolkata 700 073, India.

E Mail:

¹cskatichandan@gmail.com

²suchandra82@gmail.com

