

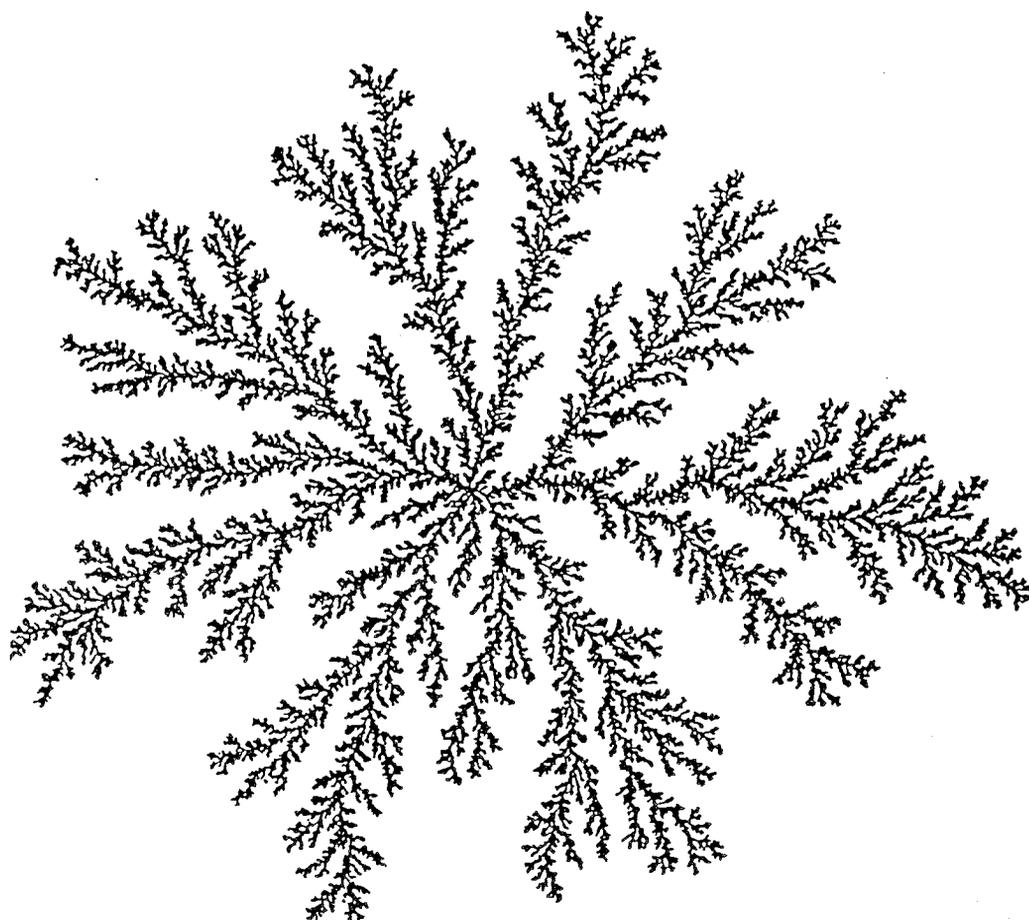
Symmetry: Culture and Science

*Symmetry and Structure:
Dialogue Among Disciplines*

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DLA fractal cluster
of 10^6 particles

SYMMETRY IN ORGANIC CHEMISTRY

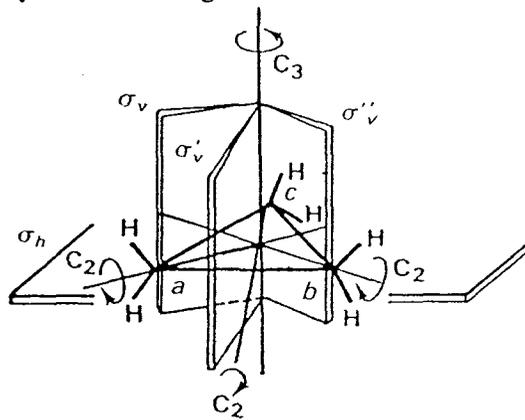
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Symmetry operations in organic chemistry give an insight into various chemical problems. They help in the understanding of the structure of organic molecules, show how atoms in a molecule are related to each other in space and also show how the individual molecules are related to one another in a crystal. The knowledge of the type of symmetry in a molecule is useful in recognising the equivalent atoms in a molecule. For example, ethane(1) (see diagram (1) in the Figures) is a symmetric molecule and there is only one possible mono-substituted ethane(2). All the six hydrogen atoms are thus chemically equivalent. Propane(3) lacks all the symmetry elements present in ethane(1) and thus all of its eight hydrogen atoms are not equivalent. Propane(3) has two different types of hydrogen atoms and gives rise to two possible monosubstituted propanes(4 and 5).

The main symmetry elements of interest to organic chemists are: points of symmetry, axes of symmetry and planes of symmetry.

Cyclopropane(6) is an interesting organic compound which has three vertical planes of symmetry σ_v and one horizontal plane of symmetry σ_h (See Figure 1). Cyclopropane also has C_3 and C_2 axes of symmetry. Substituted cyclopropanes 8b and 9 have lost all of the symmetry elements present in the parent cyclopropane(6) and are chiral molecules. The substituted cyclopropanes 7 and 8a still have certain elements of symmetry as shown in Figure 2.



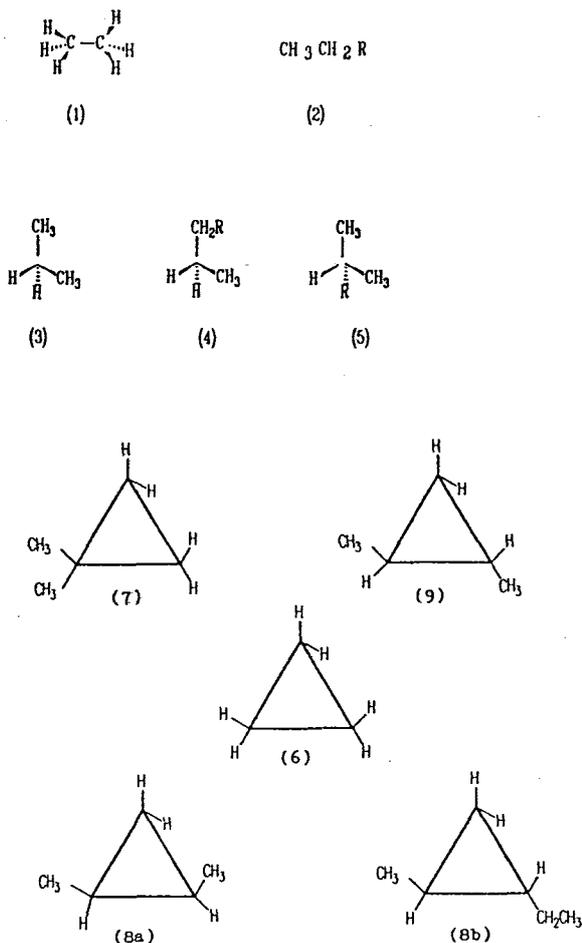
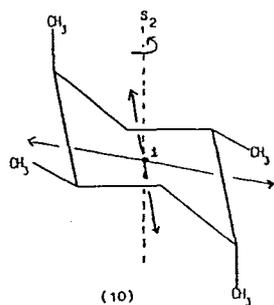


Figure 2

Centre of symmetry is best seen in cyclohexane derivative such as 10. Tetramethylcyclohexane(10) has a centre of symmetry and an improper axis of symmetry S_2 (See Figure 3). Some selected simple organic molecules and their principal elements of symmetry are given in Figure 4.



Tetramethylcyclohexane

Figure 3

Organic molecules with at least one chiral (asymmetric) carbon atom do not have any elements of symmetry. This is seen by considering the structure of glyceraldehyde(11). It has one chiral carbon atom and, as seen from its 3-dimensional model and structure (Figure 5), exists

in two spatially different forms described as D- and L-glyceraldehyde 11 and 12. Structure 13 has eight chiral atoms denoted by asterisks in 13. Two hundred and fifty six different compounds are theoretically possible for 13 and one is cholesterol whose stereochemical structure is represented in 14.

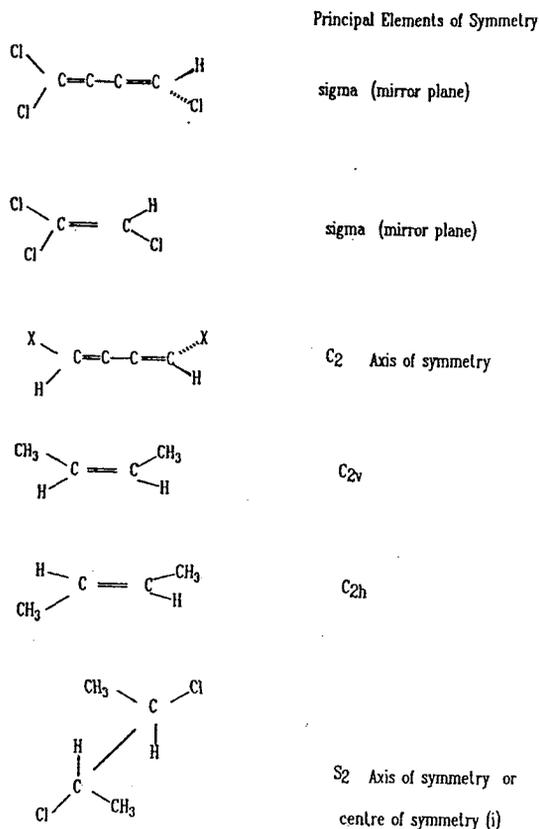


Figure 4

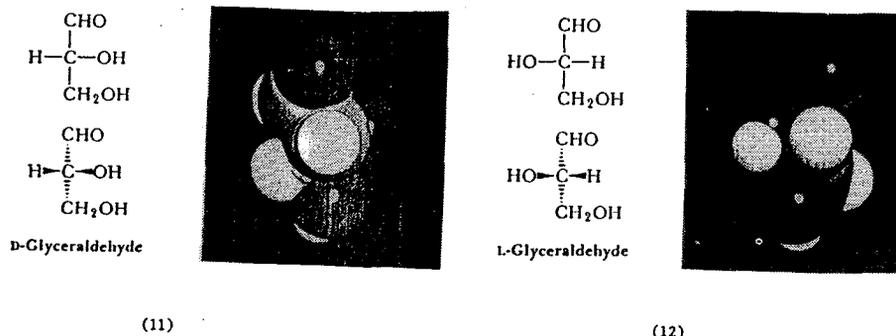
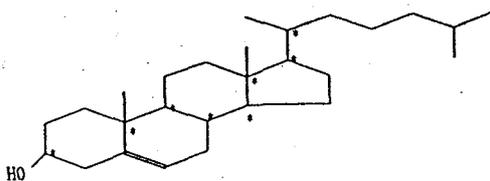
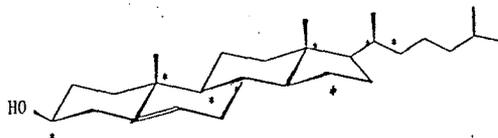


Figure 5



(13)



(14)

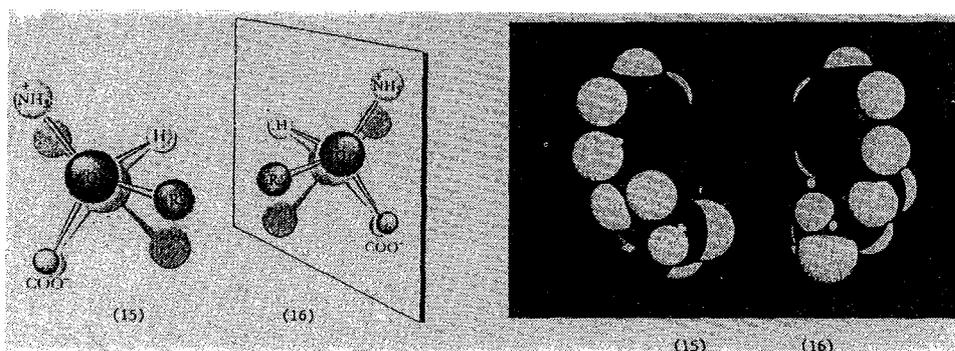


Figure 5

CHIRALITY AND MOLECULAR SYMMETRY

Achiral (not chiral) molecules have at least one element of symmetry. They are symmetric molecules and their mirror images are superimposable on the objects. Chiral molecules are those in which the objects and their corresponding mirror images are not superimposable. Chiral molecules may or may not have chiral carbon atoms. Amino acids which are the building blocks of proteins contain chiral carbon atoms (15, R=H). The object 15 and its mirror image 16 are not superimposable. The chirality of the molecule 15 is due to the presence of a chiral carbon atom. *trans*-1,2-Dimethylcyclopropane(17) is another example of a chiral molecule (See Figure 6). Chiral molecules are capable of enantiomerism and the mirror image structures are called enantiomers.

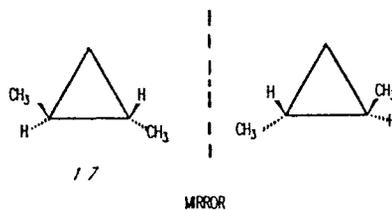
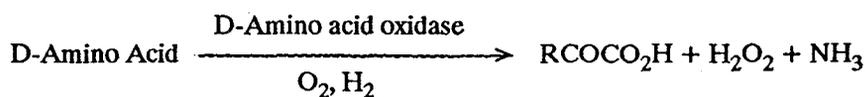
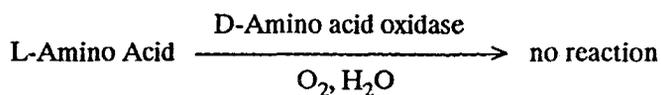


Figure 6

Enantiomers have similar chemical and physical properties but rotate the plane of polarization of plane polarized light in opposite directions to the same extent. With chiral reagents, such as the enzyme D-Amino oxidase, the enantiomeric amino acids 15 and 16 react differently:



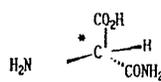
Biological activities of dissymmetric compounds are often linked to their molecular chirality. Biological activity is thus a convenient method, in some cases, for differentiating between two enantiomers. For example the amino acid D-Asparagine (18) tastes sweet whereas its enantiomer L-asparagine(19) tastes bitter. (-)Methadone (20) is a strong analgesic whereas its enantiomer (+)methadone (21) is not biologically active.

The chiral carbon atoms in asparagine and methadone are marked with asterisks.



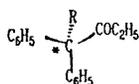
(18)

D-Asparagine



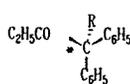
(19)

L-Asparagine



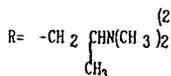
(20)

(-)-Methadone



(21)

(+) -Methadone



For the observed biological activity the enantiomer should have the correct molecular geometry and thus have the correct symmetry to interact with the active site of the biological receptor. This is shown in Figure 7.

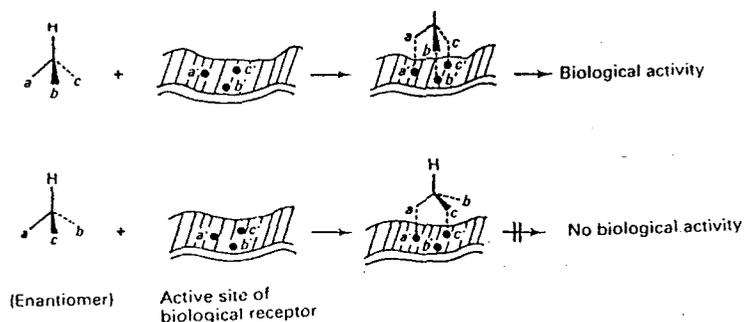


Figure 7

Proteins are built up of a large number of amino acids which have chiral atoms as explained earlier. Proteins are thus non-symmetric organic molecules. Hemoglobin which is the oxygen-carrying protein of red blood has a quaternary structure. Even though each protein molecule is non-symmetric, hemoglobin whose structure has four similar protein molecules has a symmetric structure as seen in Figure 8.

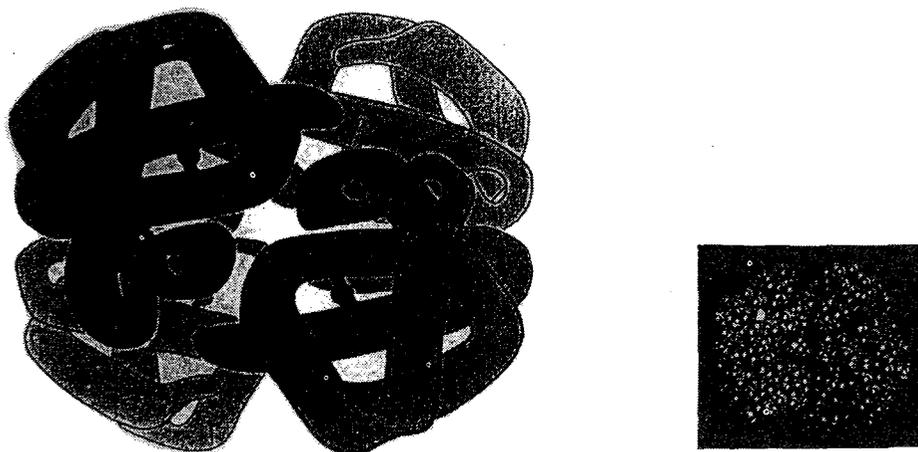


Figure 8

Acetylene and benzene are planar molecules with symmetries $D_{\infty h}$ and D_{6h} respectively (See Figure 9). Benzene possesses a C_6 axis perpendicular to the ring which contains six C_2 axes. The benzene ring is of planar symmetry σ_h . Plant phenols contain many benzene rings. In our study of plant phenols we have reviewed the biochemistry of these phenols. Resveratrol(22) is the building block for these phenols. It is planar and thus a symmetric molecule. But, hopeaphenol(23) which is built up from four resveratrol molecules is a dissymmetric molecule.

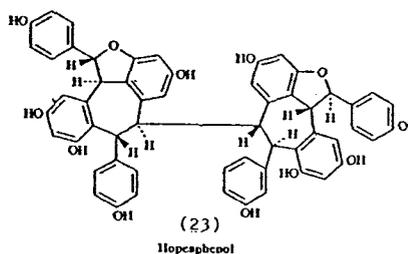
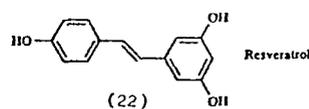
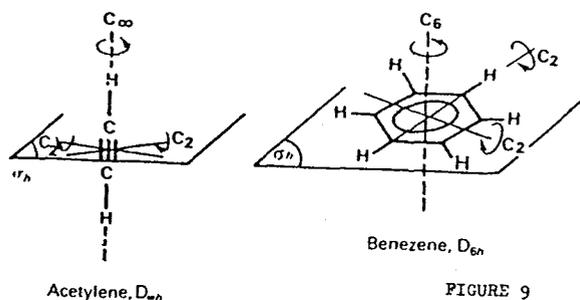


Figure 9

Many naturally occurring organic compounds which are produced by living species are asymmetric molecules. This is because these substances are produced by the organisms with certain biological activities in mind and thus should be dissymmetric molecules with correct geometries tailor made to interact with their corresponding biological receptors.

Several non-symmetrical naturally occurring organic compounds have been isolated by us, and, in a review of our work, the occurrence of several chiral polyphenols have been described (Pasupathy, Sotheeswaran, 1993).

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