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Local symmetry and chirality of molecular faces

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Abstract. The concept of local symmetry has been applied to faces of planar sites such as carbon–carbon double bonds and aromatic rings with the principal results being as follows. The two faces of a planar site must have the same local symmetry group. This local symmetry group is limited to the polar point groups. For cyclic compounds, directed cycles must have chirotopic faces although the reverse is not necessarily true: chirotopic faces are possible for both directed and undirected cycles. A number of examples are provided to illustrate these results.

Key words: Local symmetry – Chirality – Faces – Chirotopic – Directed cycles

In recent years, the application of symmetry concepts in organic synthesis has become a vigorous field of research [1]. The presence of symmetry in a complex molecule often simplifies its synthesis: a large symmetric molecule can sometimes be synthesized by the joining of two or more molecules of a "monomer". Symmetry is also an important property of reactants and synthetic intermediates: in general, a smaller number of symmetry-distinct reaction sites results in fewer different products. In connection with this, the concept of local symmetry and local chirality is of significant interest to synthetic chemists and many chemists do indeed have an intuitive awareness of this concept.

The essence of this concept has existed for a long time. More than a century ago, Curie [2] studied the relation between the symmetry of an ensemble of objects and the symmetries of the individual objects. The concept is also well established in crystallography, as evidenced by the terms "special positions" and "site symmetry" [3]. In 1984, Mislow and Siegel [4] recast the concept of local symmetry and local chirality specifically for molecular segments. In theory, this concept is applicable to all points and segments of a molecule, including faces; however, during the 16 years since the introduction of the local symmetry concept, we have not encountered any description of molecular faces in terms of their local symmetry. Here we explore the application of the local symmetry concept to the faces of planar sites, such as carbon–carbon double bonds, aromatic rings, etc., and describe their symmetry properties.

In this work, we will be concerned exclusively with approximately planar or two-faced sites such as carbon–carbon double bonds. We will not deal here with the faces of entities such as cubes or dodecahedra that may naturally be considered many-faced. This does not curtail the range of application of the present theory seriously, since molecular polyhedra (e.g. cubane, dodecahedrane, fullerenes) are relatively uncommon in organic chemistry in comparison to planar entities such as carbonyl groups or carbon–carbon double bonds.

Definition: A molecular face is the entire region (also conveniently referred to as a half-space) on either side of a single plane imagined to pass through the molecule.

The term half-space should not be interpreted too literally. A plane slices all space into two parts which we call half-spaces in the sense that, together, they span all space. The atomic or chemical contents of these half-spaces need not be the same, nor do they need to be symmetry-related.

In order that our definition of a molecular face be useful, the position of the slicing plane should be chosen in a chemically reasonable fashion. For instance, the slicing plane may be identified with the best-fit plane of the nuclei constituting the planar site; however, the choice of the slicing plane is strictly a matter of chemical convenience and it does not in any way affect the validity of the theorems stated below.

Definition: The local symmetry group of a molecular face consists of all those elements of the molecular point group whose operation leaves the face invariant or indistinguishable from its original condition.[1]

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[1] Based on the recently proven holographic electron density theorem [5], an improvement on the Hohenberg–Kohn theorem, it is now proven that local-only symmetry cannot exist and that the local (submolecular) symmetry necessarily implies global (molecular) symmetry [6]

Obviously, the position of the slicing plane will be a factor in determining what the local symmetry group of the two faces will be. The following result is slightly more subtle.

Theorem 1: A single plane (whatever its position or orientation) must divide a molecule into two faces or half-spaces whose local symmetry groups are the same.

It is important to appreciate that the local symmetry group is necessarily a subgroup of the molecular point group, i.e. a molecular segment cannot have a symmetry element that is not present in the whole molecule. A segment's local symmetry group describes its symmetry in situ, i.e. in the context of its environment within the whole molecule. A segment's local symmetry group must reflect not only the symmetry of its distribution of atomic nuclei, but also that of its electron distribution.

Proof: Let X and Y denote the two faces or half-spaces of a molecule, M. By the definition of local symmetry, every element in the local symmetry group of X and of Y must also be an element of the point group of M.

Suppose that the local symmetry group of X contains some element x_1 that is not included in the local symmetry group of Y. Operation of x_1 on the molecule will leave X invariant but will leave Y in a state distinguishable from its original one. This in turn means that operation of x_1 will leave M in a state distinguishable from its original one; however, this contradicts our accepted premise that x_1 is a symmetry operation of M. Therefore, X cannot have any element in its local symmetry group that Y does not have. In other words X and Y must have the same local symmetry group.

As a practical illustration of this theorem, we can consider the double bond epoxidation reaction. Theorem 1 implies that the epoxide products resulting from epoxidation of the two faces of an arbitrary double bond should have the same molecular point groups.[2] This result holds regardless of whether the faces of the substrate double bond are homotopic, for example, ethylene or (*Z*)-2-butene, enantiotopic, for example, (*E*)-2-butene, or symmetry-distinct, for example, norbornene.

A pertinent question at this point is whether any limitations to the local symmetry groups are possible for the faces of planar sites. It is easy to find by inspection and it is also intuitively reasonable that the two faces of a carbon–carbon double bond can never have local symmetry groups such as O_h, T_d, or D_n. Indeed, only certain local symmetry groups are possible for a generic molecular face. To state this precisely, we recapitulate the definition of a polar point group.

Definition [7]: A polar point group is one which does not include the following symmetry elements or combinations of symmetry elements.

1. An inversion center ($i = S_2$).
2. An improper axis of symmetry, $S_n (n > 2)$.
3. Intersecting proper axes of symmetry.
4. A plane of symmetry intersecting a proper axis.

It is easy to see that the presence of these symmetry elements precludes the presence of an electric dipole moment in the molecule. The following point groups are polar: C_1, C_n $(n > 1)$, C_s, and C_{nv} $(n > 1)$.

Theorem 2: The local symmetry group of a molecular face must be a polar point group.

Proof: We remind ourselves that a molecular face, symbolized X, is the entire space, including its chemical content (i.e. electrons and atomic nuclei), on either side of an imaginary plane, P, slicing a molecule, M. Let H_x be the local symmetry group of the face X.

The maximum symmetry of a plane, embedded in isotropic three-dimensional space, about an arbitrary point is $D_{\infty h}$, and this holds when the point lies in the plane (the C_∞ axis being perpendicular to the plane). The subgroup of symmetry operations of this $D_{\infty h}$ group, under which the plane's two sides are not interchanged, is $C_{\infty v}$.

Since the plane P is the boundary surface of the face X, P must remain invariant under every symmetry operation of the local symmetry group H_x. Also, the two sides of P must not be interchanged under any symmetry operation of the group H_x. Therefore, in view of the last paragraph, H_x must be a subgroup of $C_{\infty v}$, which is itself a polar group. (The face X in general has lower symmetry than $C_{\infty v}$ because of the symmetry-lowering effect of its chemical content.) X is therefore limited to C_1, C_n $(n > 1)$, C_s, and C_{nv} $(n > 1)$.

Following established terminology [4], we designate faces with chiral local symmetries as chirotopic and those with achiral local symmetries as achirotopic. From theorem 2, we see that the local symmetries possible for chirotopic faces are C_1 or C_n $(n \geq 1)$ and those possible for achirotopic faces are C_s and C_{nv} $(n \geq 1)$. In other words, the local symmetry groups possible for the faces of planar sites are quite limited. Since a chiral molecular point group cannot have an achiral local symmetry group as its subgroup, only achiral molecules can have achirotopic faces. Chirotopic faces can be present in both achiral and chiral molecules.

As an interesting example of molecular facial symmetry, let us consider the chiral complex, tricarbonyl[hexakis(dimethylsilyl)benzene]chromium, reported by Mislow and coworkers [7]. The special characteristic of the hexakis(dimethylsilyl)benzene ligand is that steric congestion forces all the dimethylsilyl groups to point in the same direction, resulting in a "gear-meshed" C_{6h} molecular geometry, as distinct from the D_{6h} symmetry of benzene, and chirotopic C_6-symmetric arene faces. Tricarbonyl[hexakis(dimethylsilyl)benzene]chromium was found to have perfect crystallographic C_3 symmetry.

Finally, we examine the facial symmetries of cyclic molecules. According to Mislow [7], "a cycle is defined by three or more non-collinear points in the molecule. A cycle is undirected if it is bisected by a molecular C_{2n} axis in, or by a molecular s plane perpendicular to, the mean plane of the cycle. Otherwise it is directed." Thus the benzene ring in the hexakis(dimethylsilyl)benzene is a

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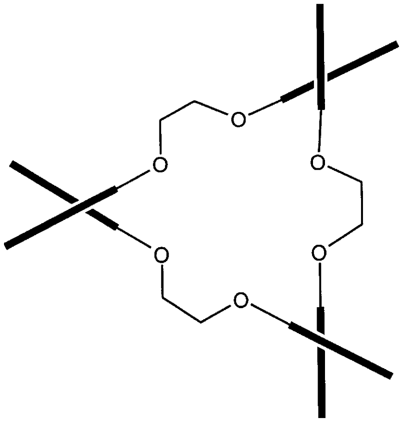
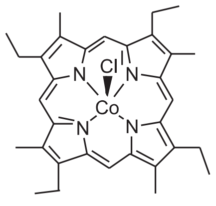
[2] More precisely, this statement must hold except in the rather uncommon case that the epoxidation introduces a new symmetry element in the molecule

directed cycle. We define a cycle's face as the entire region (or half-space) on either side of the mean plane of the cycle.

Because a directed cycle cannot be bisected by a C_{2n} axis, it can only have enantiotopic or symmetry-distinct faces, but not homotopic ones. Similarly, an undirected cycle can only have homotopic or symmetry-distinct faces, but not enantiotopic ones. A face of an undirected cycle may belong to any of the local symmetry groups, C_1, C_n ($n > 1$), C_s, or C_{nv} ($n > 1$); however, since a directed cycle must not be bisected by mirror planes perpendicular to its mean plane, its faces cannot belong to the local symmetry groups C_s or C_{nv} ($n > 1$). We thus arrive at the interesting result that a directed cycle must have chirotopic faces of local symmetry groups C_1 or C_n ($n > 1$). The converse, however, is not true: a cycle with chirotopic faces is not necessarily directed. For instance, the six oxygen atoms of the 2,2′-binaphthyl-based D_3-symmetric crown ether (depicted below) may be regarded as an undirected cycle (on account of the molecular C_2 axes), but the faces of this cycle are chirotopic with C_3 local symmetry. [8]

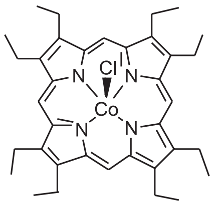


An interesting case of cyclic directionality is furnished by some chiral cobalt etioporphyrin I complexes prepared by Konishi et al. [9] in the course of a study on the mechanism of transfer of alkyl and aryl groups between cobalt and nitrogen. A four-coordinate metal complex (i.e. without axial ligands) of etioporphyrin I has time-averaged C_{4h} symmetry and therefore has enantiotopic faces. This contrasts with the octaethylporphyrinato ligand, which has time-averaged D_{4h} symmetry and achirotopic C_{4v}-symmetric faces. The cyclic directionality of the etioporphyrin I ligand translates directly into the chirotopicity of its faces and the chirality and enantiomerism of its Co^{III}-Cl complexes, as depicted below.



Co^{III}(etioporphyrin I)Cl

C_4



Co^{III}(Octaethylporphyrinato)Cl

C_{4v}

In summary, we have applied the concept of local symmetry to molecular faces and found that they have some simple symmetry properties. It is hoped that wider appreciation of symmetry concepts such as those formulated here will stimulate organic chemists to further exploit symmetry in their synthetic work.

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