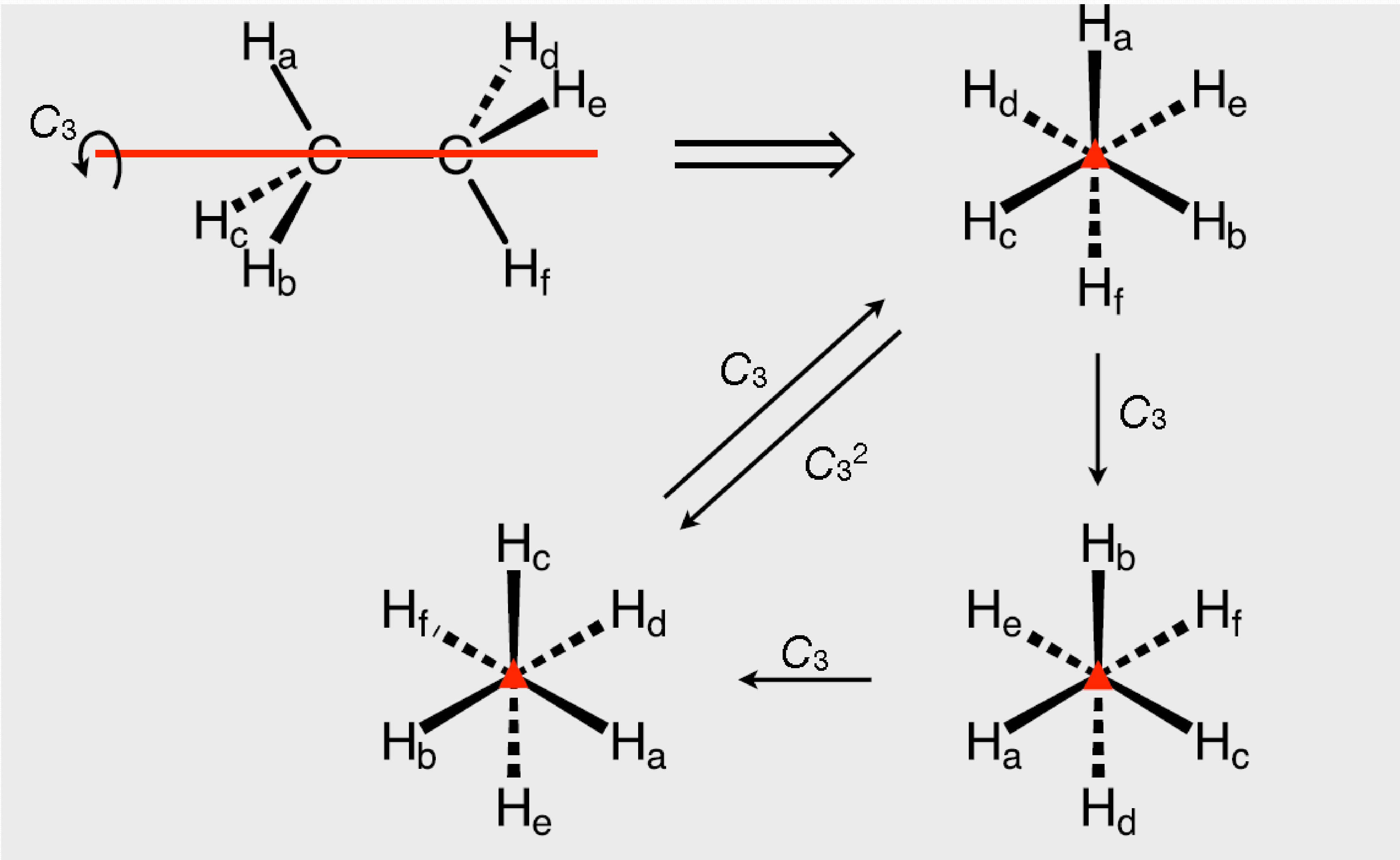
Symmetry and Point Groups

Chapter 4

Monday, September 28, 2015

Symmetry in Molecules: Staggered Ethane



So far we can say staggered ethane has three operations: E, C_3, and C_3^2

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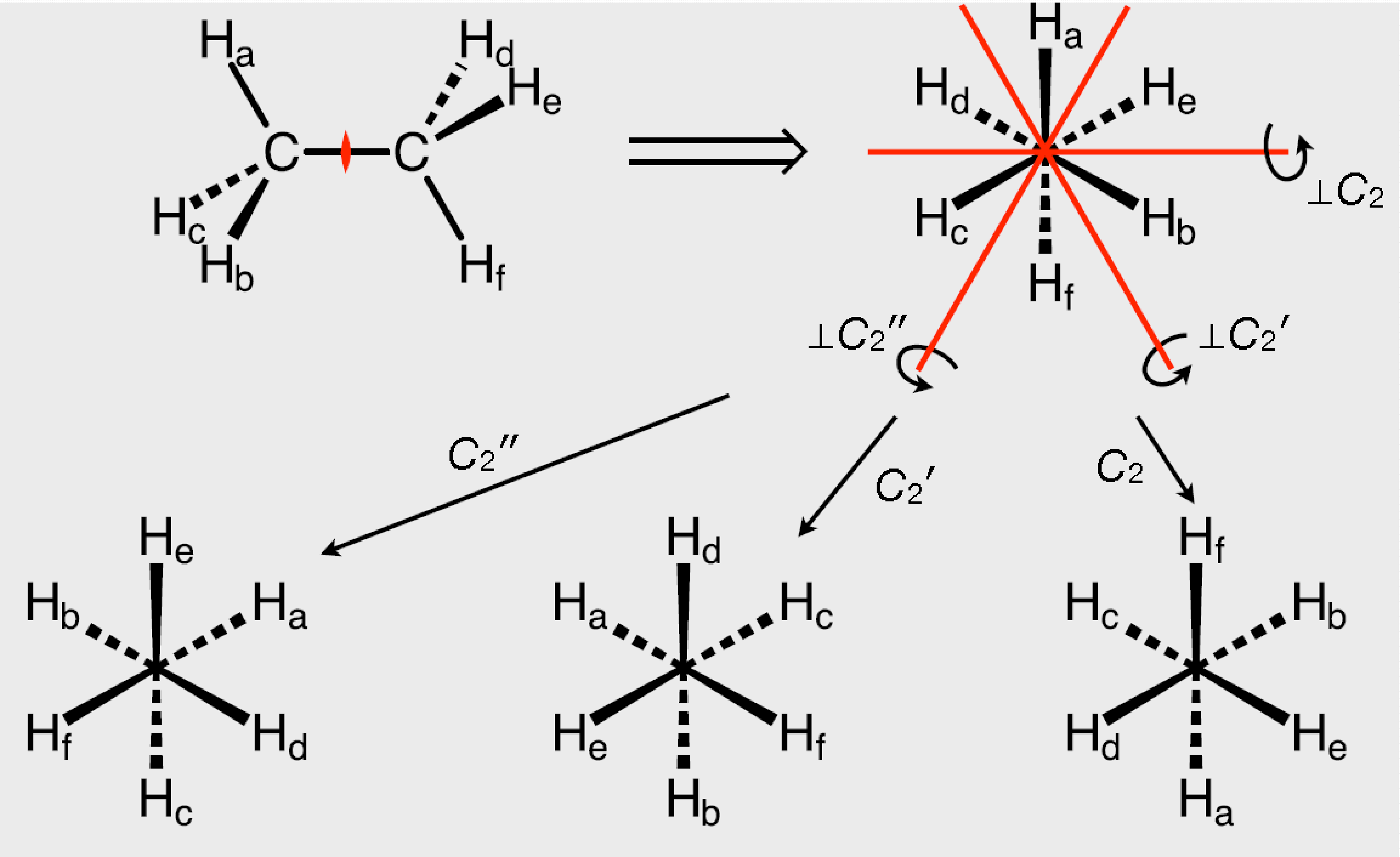
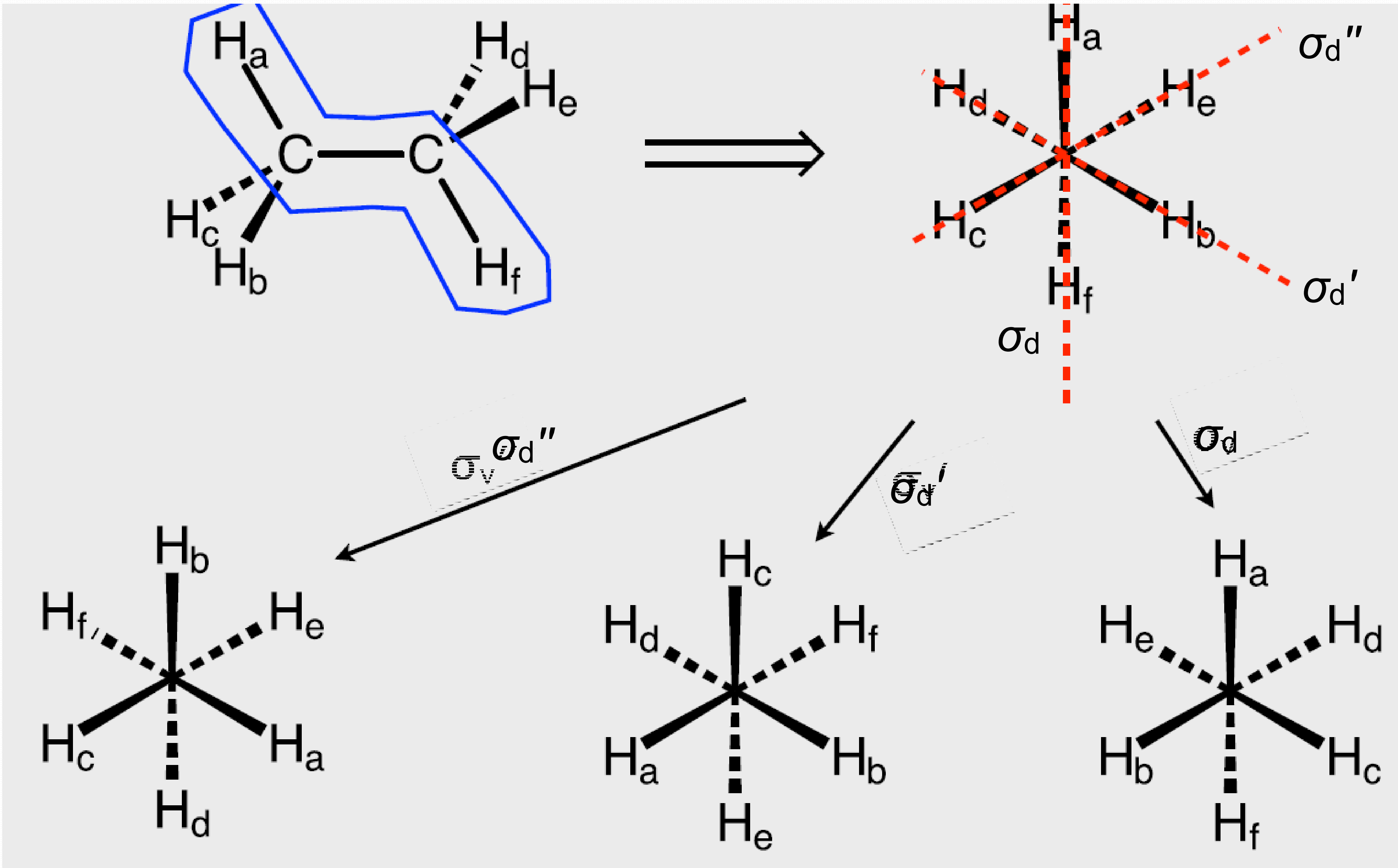


So we add three more operations: C_2, C_2', and C_2''

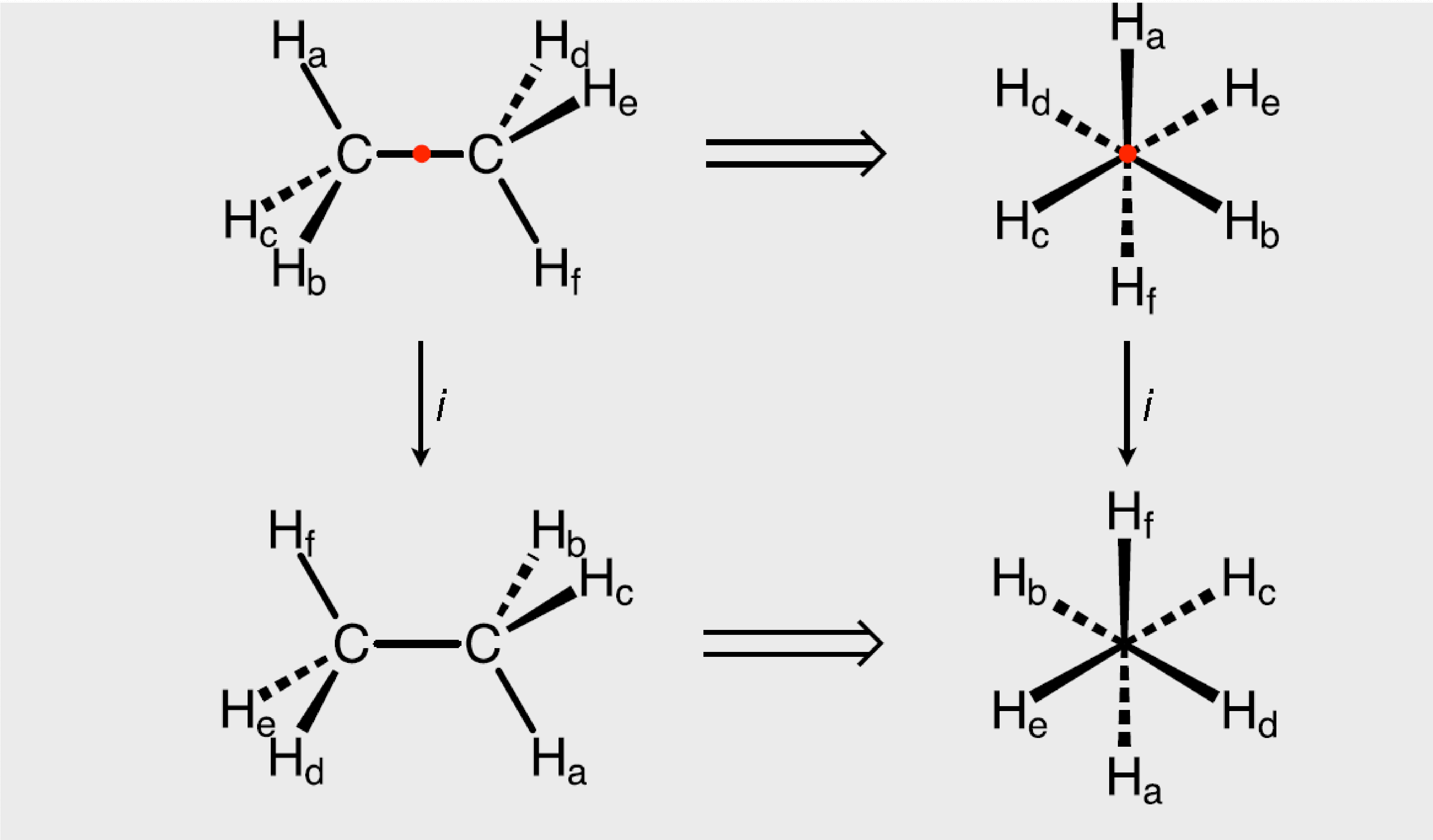
Symmetry in Molecules: Staggered Ethane



Now we've added three reflections: σ_d, σ_d', and σ_d''

Note that there is no σ_h for staggered ethane!

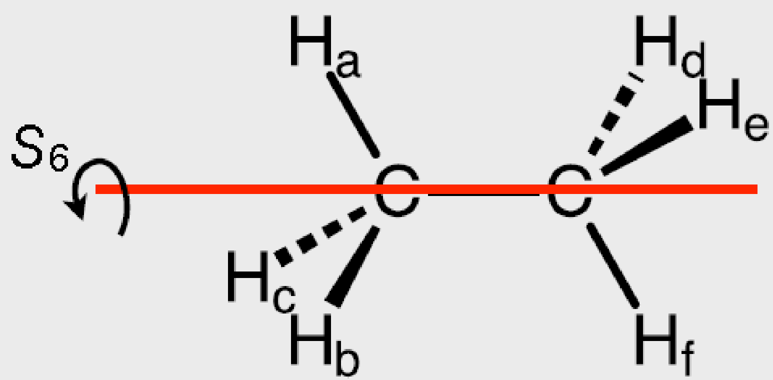
Symmetry in Molecules: Staggered Ethane



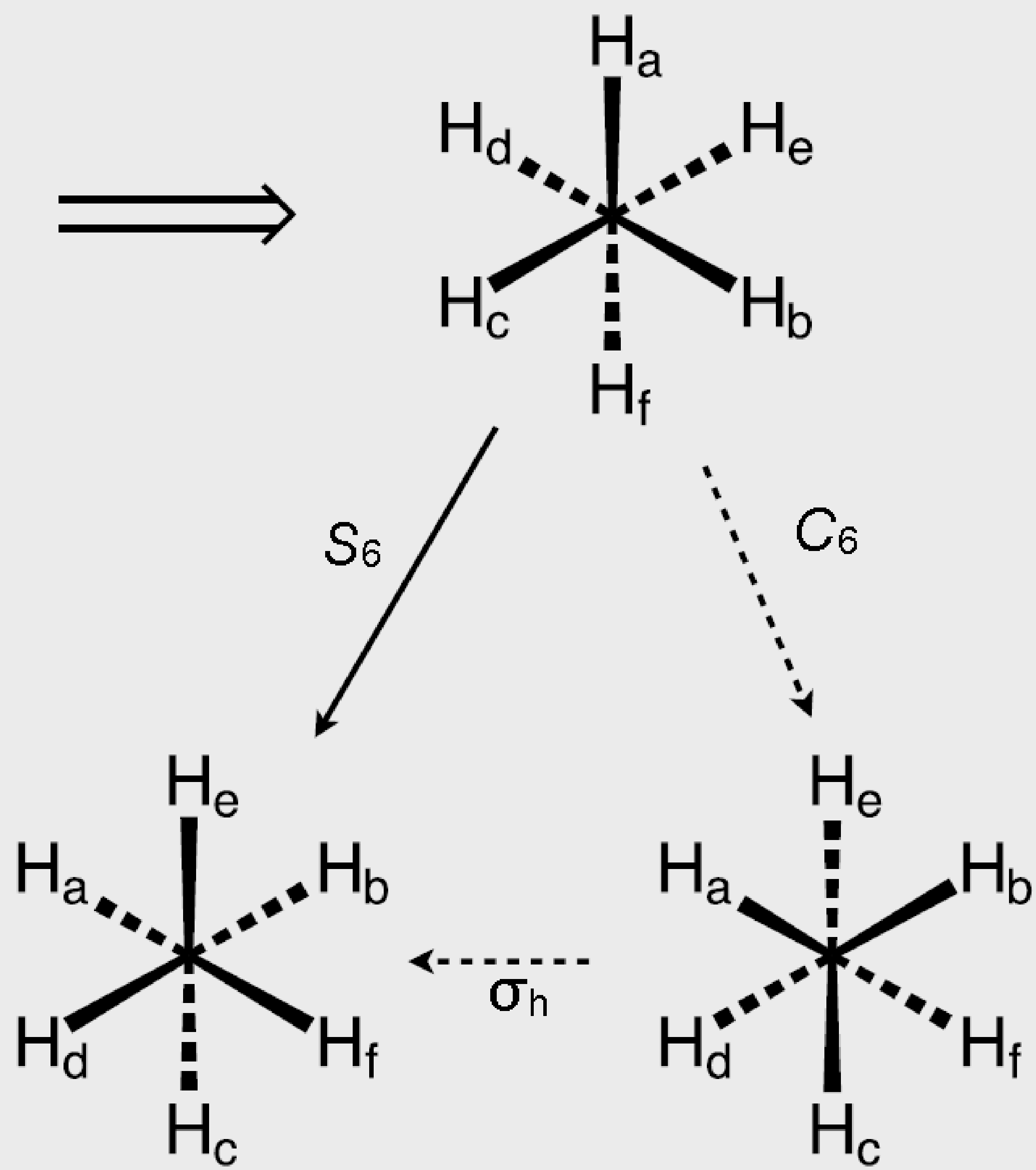
Ethane also has an inversion center that lies at the midpoint of the C-C bond (the center of the molecule).

Symmetry in Molecules: Staggered Ethane

Finally, staggered ethane also has an improper rotation axis.
It is an S_6 (S_{2n}) axis that is coincident with the C_3 axis.



An S_6 rotation is a combination of a C_6 followed by a perpendicular reflection (i.e., a σ_h).



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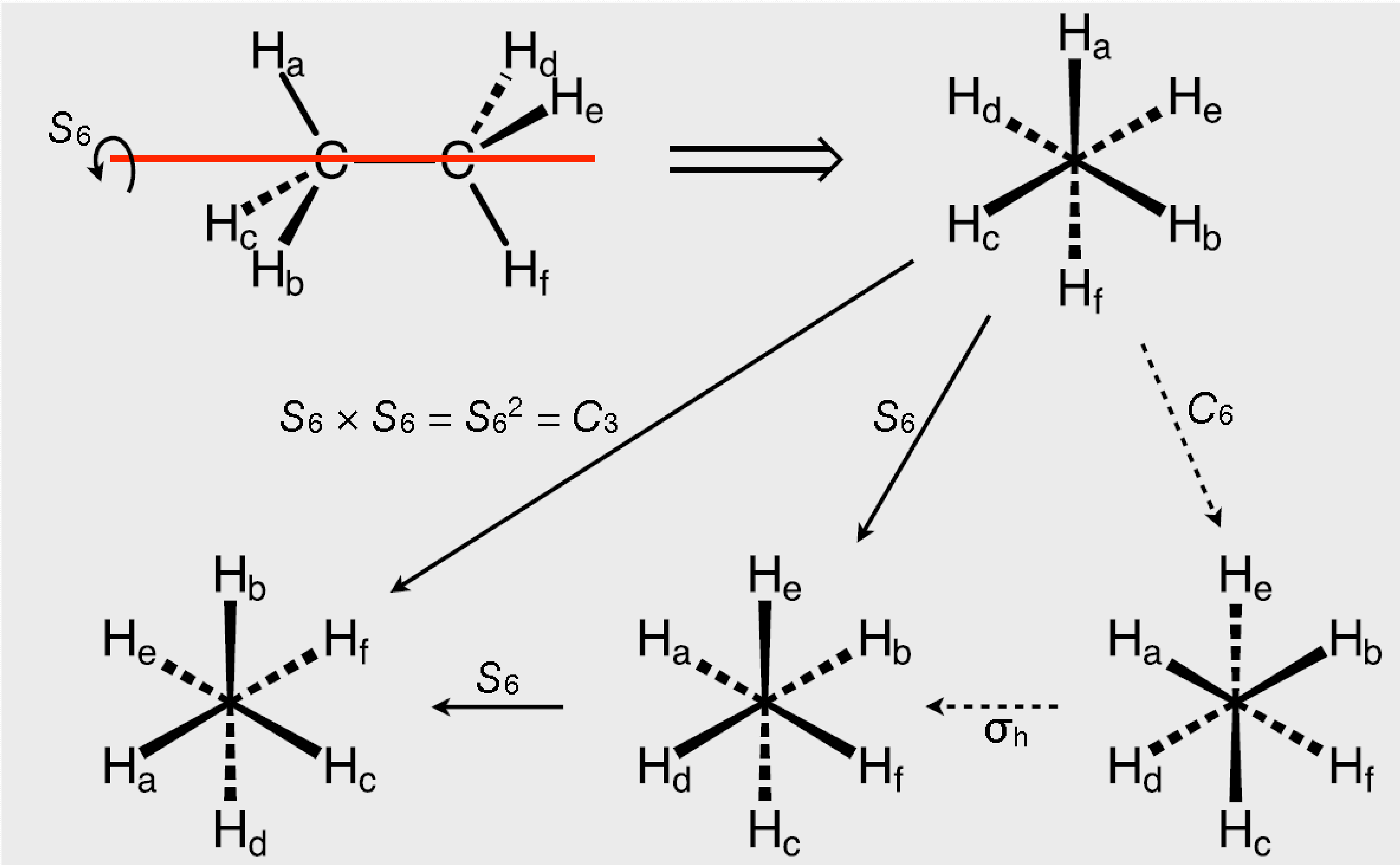
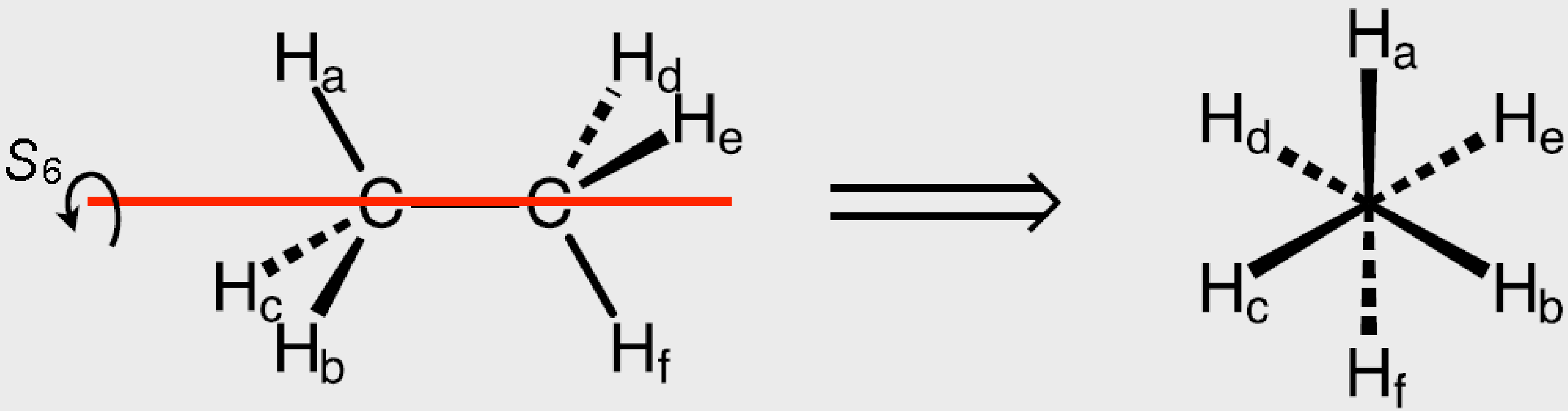


Symmetry in Molecules: Staggered Ethane

It turns out that there are several redundancies when counting up the unique improper rotations:

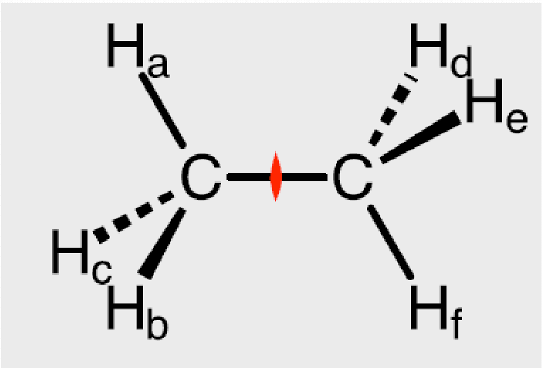


S_6 operation	equivalent operation
S_6	S_6
S_6^2	C_3
S_6^3	i
S_6^4	C_3^2
S_6^5	S_6^5
S_6^6	E

So the improper rotations add only two unique operations.

Symmetry in Molecules: Staggered Ethane

Let's sum up the symmetry operations for staggered ethane:



Operation type	Number
Identity	**1**
Rotations	**5** ($2C_3 + 3C_2$)
Reflections	**3** ($3\sigma_d$)
Inversion	**1**
Improper Rotations	**2** ($S_6 + S_6^5$)
Total	**12**

- These 12 symmetry operations describe completely and without redundancy the symmetry properties of the staggered ethane molecule.
- The complete set of symmetry operations possessed by an object defines its *point group*. For example, the point group of staggered ethane is D_{3d}.
- The total number of operations is called the *order* (h) of a point group. The order is always an integer multiple of n of the principal axis. For staggered ethane, $h = 4n$ ($4 \times 3 = 12$).

Summary

Symmetry Elements and Operations

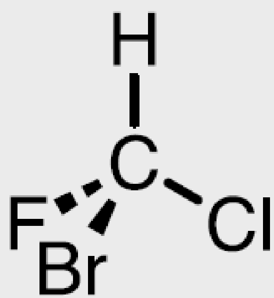
- elements are imaginary points, lines, or planes within the object.
- operations are movements that take an object between equivalent configurations – indistinguishable from the original configuration, although not necessarily identical to it.
- for molecules we use "point" symmetry operations, which include rotations, reflections, inversion, improper rotations, and the identity. At least one point remains stationary in a point operation.
- some symmetry operations are redundant (e.g., $S_6^2 \equiv C_3$); in these cases, the convention is to list the simpler operation.

Low-Symmetry Point Groups

These point groups only contain one or two symmetry operations

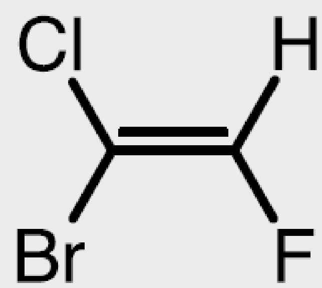
C_1

$\{E\}$



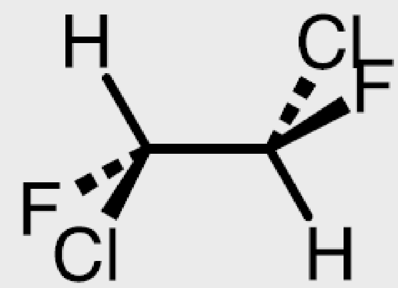
C_s

$\{E, \sigma_h\}$



C_i

$\{E, i\}$



High-Symmetry Point Groups

These point groups are high-symmetry groups derived from Platonic solids

T_d

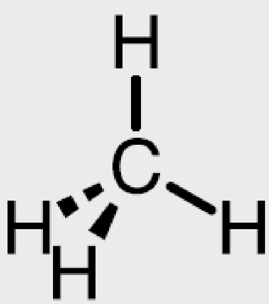
$\{E, 8C_3, 3C_2, 6S_4, 6\sigma_d\} = 24$

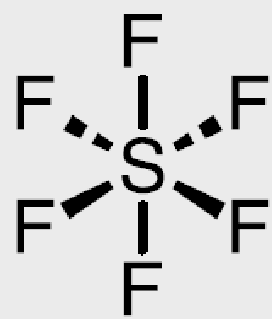
O_h

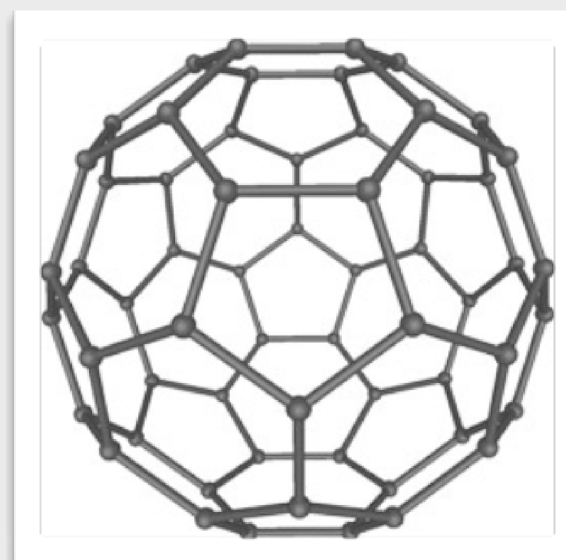
$\{E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d\} = 48$

I_h

$\{E, 12C_5, 12C_5^2, 20C_3, 15C_2, i, 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma\} = 120$







Buckminsterfullerene (C_{60})

The five regular Platonic solids are the tetrahedron (T_d), octahedron (O_h), cube (O_h), dodecahedron (I_h), and icosahedron (I_h)

High-Symmetry Point Groups

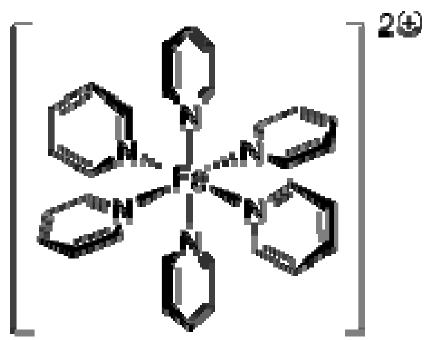
In addition to T_d, O_h, and I_h, there are corresponding point groups that lack the mirror planes (*T*, *O*, and *I*).

Adding an inversion center to the *T* point group gives the T_h point group.

TABLE 4.5 Symmetry Operations for High-Symmetry Point Groups and Their Rotational Subgroups

Point Group	Symmetry Operations									
I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(\equiv C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(\equiv C_4^2)$					
T_d	E	$8C_3$	$3C_2$				$6S_4$			$6\sigma_d$
T	E	$4C_3$ $4C_3^2$	$3C_2$							
T_h	E	$4C_3$ $4C_3^2$	$3C_2$			i	$4S_6$	$4S_6^5$	$3\sigma_h$	

T_h example:



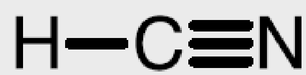
$Fe[(C_5H_5N)_6]^{2+}$

Linear Point Groups

These point groups have a C_∞ axis as the principal rotation axis

$C_{\infty v}$

$\{E, 2C_\infty^\phi, \cdots, \infty\sigma_v\}$



$D_{\infty h}$

$\{E, 2C_\infty^\phi, \cdots, \infty C_2, i, 2S_\infty^\phi, \infty\sigma_v\}$

D Point Groups

These point groups have nC_2 axes perpendicular to a principal axis (C_n)

D_n

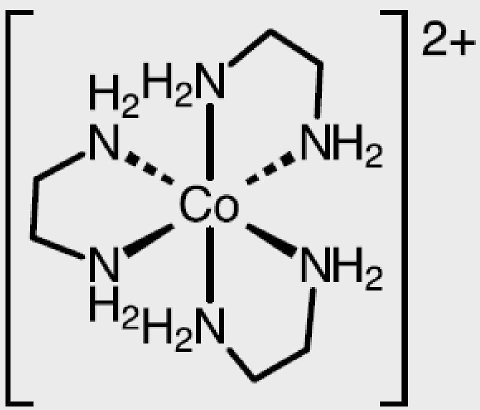
$\{E, (n\text{-}1)C_n, n\perp C_2\}$

D_{nh}

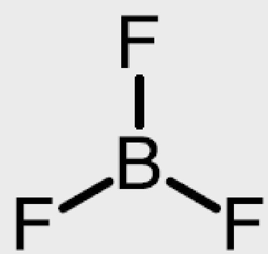
{*depends on n, with h = 4n*}

D_{nd}

{*depends on n, with h = 4n*}

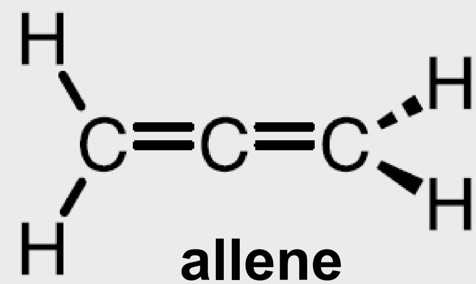


D_3



D_{3h}

$\{E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v\}$



allene (propadiene)

D_{2d}

$\{E, 2S_4, C_2, 2C_2', 2\sigma_d\}$

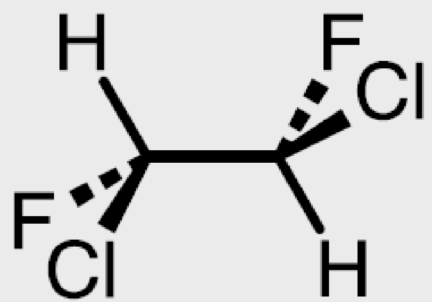
C Point Groups

These point groups have a principal axis (C_n) but no $\perp C_2$ axes

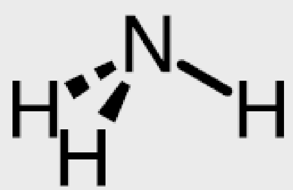
C_n
$\{E, (n\text{-}1)C_n\}$

C_{nv}
$\{E, (n\text{-}1)C_n, n\sigma_v\}$

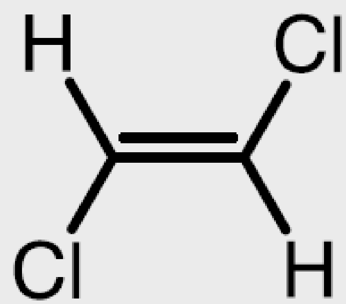
C_{nh}
{*depends on n, with h = 2n*}



C_2
$\{E, C_2\}$



C_{3v}
$\{E, 2C_3, 3\sigma_v\}$



C_{2h}
$\{E, C_2, i, \sigma_h\}$

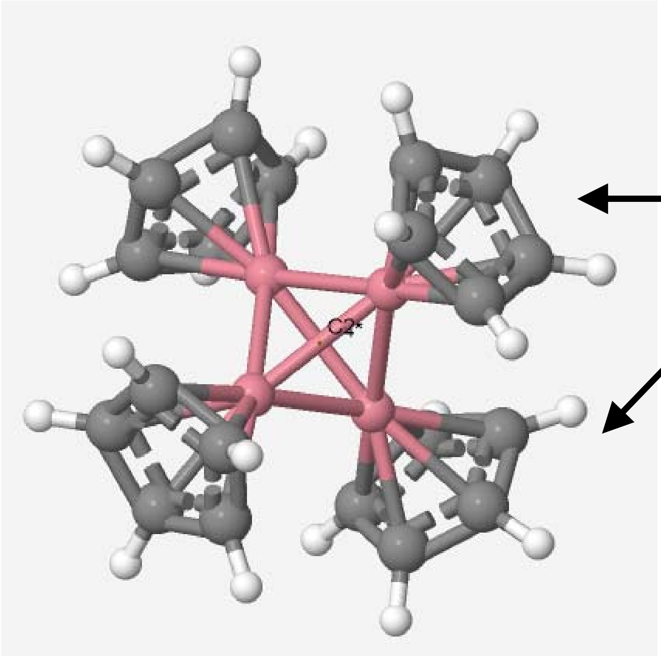
S Point Groups

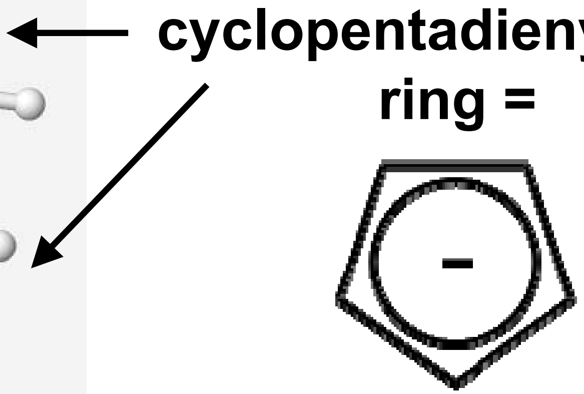
If an object has a principal axis (C_n) and an S_{2n} axis but no $\perp C_2$ axes and no mirror planes, it falls into an S_{2n} group

S_{2n}

{*depends on n, with h = 2n*}

Co_4Cp_4





S_4

$\{E, S_4, C_2, S_4^3\}$