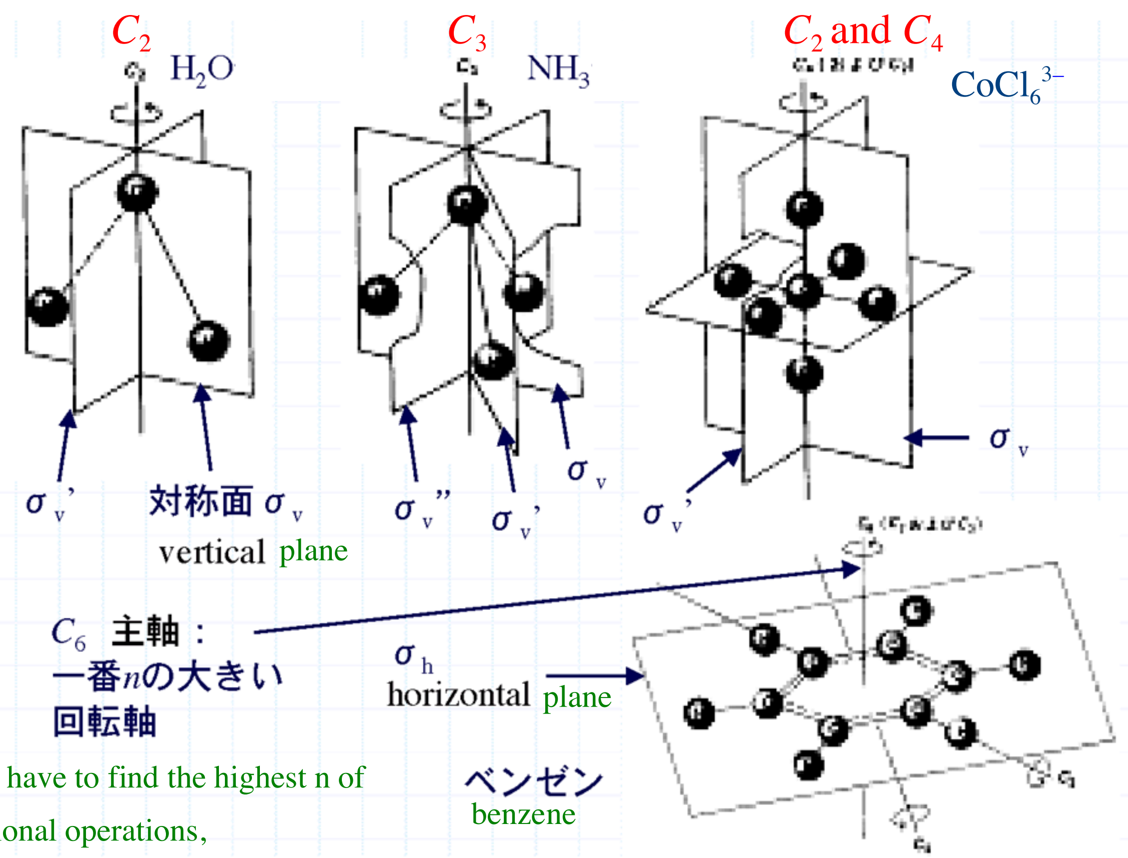
How to find symmetry and symmetry operations?

The inversion center, mirror (reflection) plane, rotation axis etc. are located within a molecule.

A molecule after operation must be identical to the original molecule.

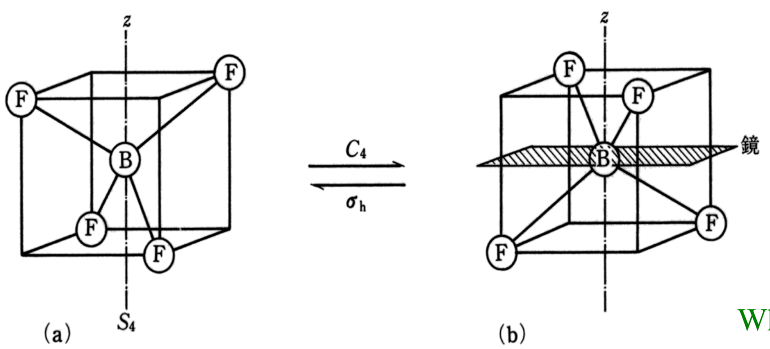
"n" in C_n is defined with the operation rotated by 360°/n.



You have to find the highest n of rotaional operations,

and you call this axis "unique" or "z".

S_n is another symmetry operation but it is synthesized from "rotation-reflection."



初めの配置(a)を z 軸を中心に 90° 回転させると(b)の配置となる．
(b)の鏡の面は対象面(σ_h)である

What is the operation S_4?

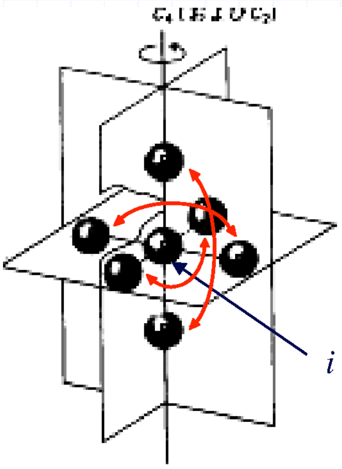
Reflection with respect to σ_h after C_4 with respect to z.

Namely, $S_4 = \sigma_h \bullet C_4$.

Please confirm $C_2 = S_4^2$.

演習　Drill

対称中心(反転)　i　inversion



座標で表わすと　in vector expression

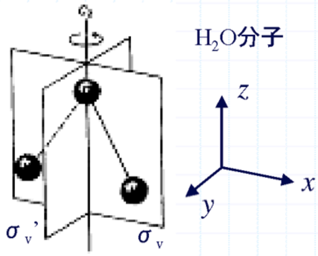
$(x, y, z) \rightarrow (-x, -y, -z)$

cf.

$\sigma\ (//xy)\quad (x, y, -z)$

$C_2\ (//z)\quad [\qquad\qquad]$

対称操作を2回続けて行った結果は別の対称操作と同じになる。　operation after operation gives a new operation.



後　　先

$C_3^{+} \times C_3^{+} = [\qquad]$

$C_3^{-} \times C_3^{+} = [\qquad]$

恒等変換(動かさない)
identical (no operation)

$\sigma_v \qquad\qquad \sigma_v'$

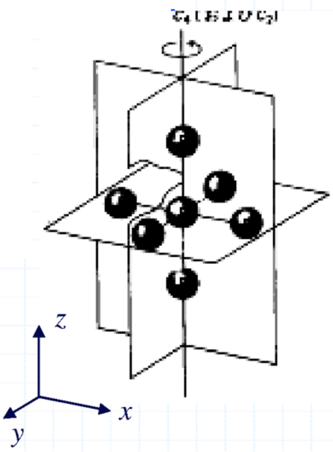
$(x, y, z) \rightarrow (x, -y, z) \rightarrow [\qquad\qquad]$

$[\qquad]$

$\sigma_v' \times \sigma_v = [\qquad]$

operation after operation gives a new operation.

対称操作を2回続けて行った結果は別の対称操作と同じになる。



座標で表わすと　in vector expression

$(x, y, z) \rightarrow$

i	$(-x, -y, -z)$
$\sigma\ (//xy)$	$(x, y, -z)$
$C_2\ (//z)$	$(-x, -y, z)$

$\sigma_v(//x) \qquad \sigma_v(//y)$

$(x, y, z) \rightarrow (-x, y, z) \rightarrow (-x, -y, z)$

$C_2(//z)$

$\sigma_v(//y) \times \sigma_v(//x) = C_2$

$\sigma_v(//x)\ \sigma_v(//y)\ \sigma_v(//z)$

$(x, y, z) \rightarrow \quad \rightarrow \quad \rightarrow [\qquad\qquad]$

$\sigma_v(//z) \times \sigma_v(//y) \times \sigma_v(//x) = [\qquad]$

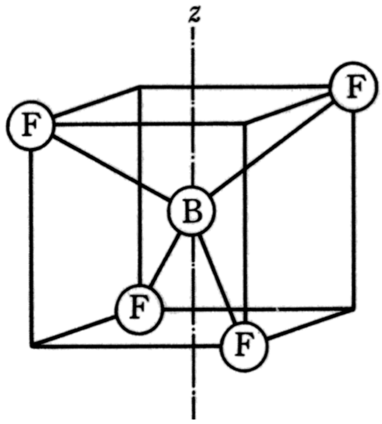
Point Group. 点群

"Group" in mathematically meaning:

the product of an element and an element must be an element in the subset. The group is closed.

要素と要素の積はその集合内の要素でなければならない。群は閉じている。

A tetrahedron: point group T_d



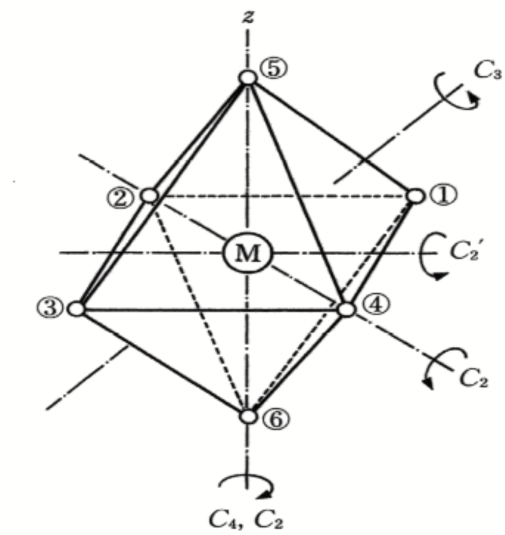
正四面体型と正八面体型錯体の対称性を調べると，非常に高い対称性をもっていることがわかる．正四面体型は対称面 σ_d をもっているので，T_d で示されるが，対称要素と対称操作の数は次のようになる．

symmetry element	対称要素	C_3	C_2	S_4	σ_d	E	
the number of symmetry elements	操作の数	8	3	6	6	1	24(合計)

ここで，E は操作しない操作（恒等操作）である．正四面体型錯体の対称操作は 24

E: identity or no operation

An octahedron: point group O_h



symmetry element	対称要素	C_3	C_2'	C_4	C_2	i	S_4	S_6	σ_h	σ_d	E	
the number of symmetry elements	操作の数	8	6	6	3	1	6	8	3	6	1	48(合計)

このように，正八面体型錯体の場合には 48 個の対称操作が存在し，きわめて高い対称性をもっていることがわかる．

Table of **Five-types** of symmetry elements, operations, and symbols.

Element	Operation	Symbol
Identity	identity	Q1
Proper axis 本義回転	rotation by (360/n)°	Q2
Symmetry plane	reflection in the plane	Q3
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	Q4
Improper axis 転義回転 (Alternating axis)	rotation by (360/n)°, followed by reflection in the plane perpendicular to the rotation axis 回映	Q5

$C_1 =$ E

$S_1 =$ Q6

$S_2 =$ Q7

What is “Chiral”？ キラル（化学）、カイラル（物理）

If a molecule belongs to a chiral point group, then it has a mirror image that cannot be superimposed with the original molecule. The two mirror images are called enantiomers.

Chiral point groups are classified into two: (1) chiral groups and (2) purely rotational groups.

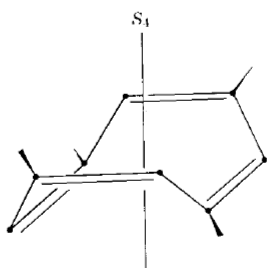
(1) point group C_1 (which has E as an only element). Many biological molecules.

(2) C_n, D_n, T, O

“Molecules without S_n symmetry are chiral.”

2-blade propeller：
two C_2’s perpendicular $C_2(z)$
→ point group D_2
→ chiral (case 2)

screw：
no C_2’ perpendicular C_4
→ point group C_4
→ chiral (case 2)



1,3,5,7-tetrachloro-1,3,5,7-cyclooctatetraene
Only S_4 symmetry is found.
→ point group S_4
→ achiral （キラルでない）
No σ, no i. But the mirror image is superimposed to original one.

Nomenclature/Classification of point groups

点群の種類

Schönflies記号

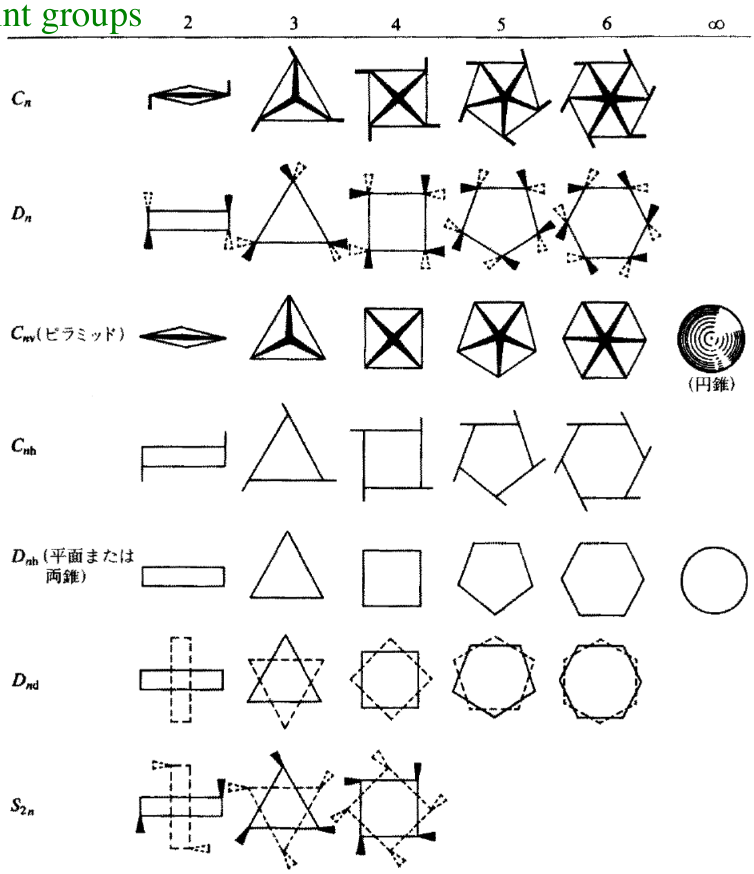
C_{2v}

for molecules, point group (分子、点群)

~~Hermann-Mauguin記号~~

~~2/m~~

~~for crystals, space group (結晶、空間群)~~



Example　　　　operations (E is excluded.)

点群の記号とこれらの点群に含まれる恒等操作Eを除く対称操作の例†

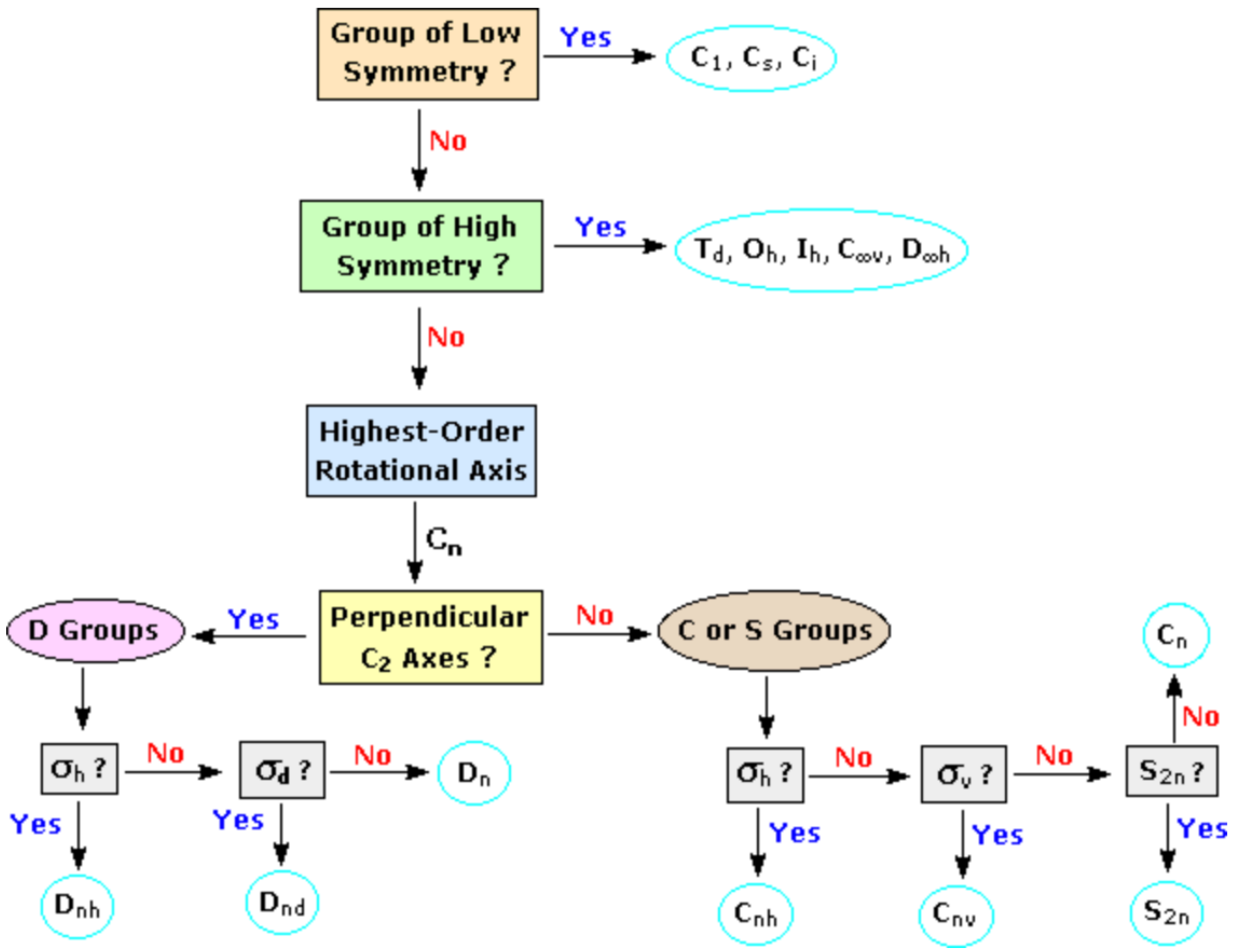
	C_s	NOCl	σ_h
	C_2	H_2O_2	C_2
	C_{2v}	H_2O	$C_2(z)$, $\sigma_v(xz)$, $\sigma_v'(yz)$
	C_{2h}	*trans*-$C_2H_2Cl_2$	$C_2(z)$, $\sigma_h(xy)$, i
	C_{3v}	NH_3	$2C_3(z)$, $3\sigma_v$
	C_{4v}	B_5H_9	$2C_4(z)$, $C_2(z)$, $2\sigma_v$, $2\sigma_d$
	C_{6v}		$2C_6(z)$, $2C_3(z)$, $C_2(z)$, $3\sigma_v$, $3\sigma_d$
$H_2C{=}C{=}CH_2$	D_{2d}	アレン allene	$C_2(z)$; $2S_4(z)$, $2C_2$(x および y), $2\sigma_d$
$H_2C{=}CH_2$	D_{2h}	エチレン ethylene	$C_2(x)$, $C_2(y)$, $C_2(z)$, i, σ_{xy}, σ_{xz}, σ_{yz}
cyclohexane	D_{3d}	シクロヘキサン	$2C_3(z)$, $2S_6(z)$, $3C_2$(zに対して⊥), i, $3\sigma_d$
cyclopropane	D_{3h}	シクロプロパン	$2C_3(z)$, $2S_3(z)$, $3C_2$(zに対して⊥), σ_h, $3\sigma_v$
cyclobutane	D_{4h}	シクロブタン	$2C_4(z)$, $C_2(z)$, $2S_4(z)$, $2C_2''$(zに対して⊥), $2C_2'$(zに対して⊥), i, $2\sigma_v'$, $2\sigma_v''$, σ_h
benzene	D_{6h}	ベンゼン	$2C_6(z)$, $2C_3(z)$, $C_2(z)$, $2S_6(z)$, $2S_3(z)$, $3C_2$(zに対して⊥), $3C_2'$(zに対して⊥), i, σ_h, $3\sigma_v$, $3\sigma_d$
methane	T_d	メタン	$8C_3$, $6S_4$, $3C_2(=3S_4^2)$, $6\sigma_d$
	O_h	SF_6	$6C_4(x,y,z)$, $3C_2(x,y,z)$, $6S_4(x,y,z)$, $8C_3$(diag), $8S_6$(diag), $6C_2$, $3\sigma_h$, $6\sigma_d$, i

† z軸が垂直方向にあると仮定する. On the assumption of z-axis in a vertical direction.

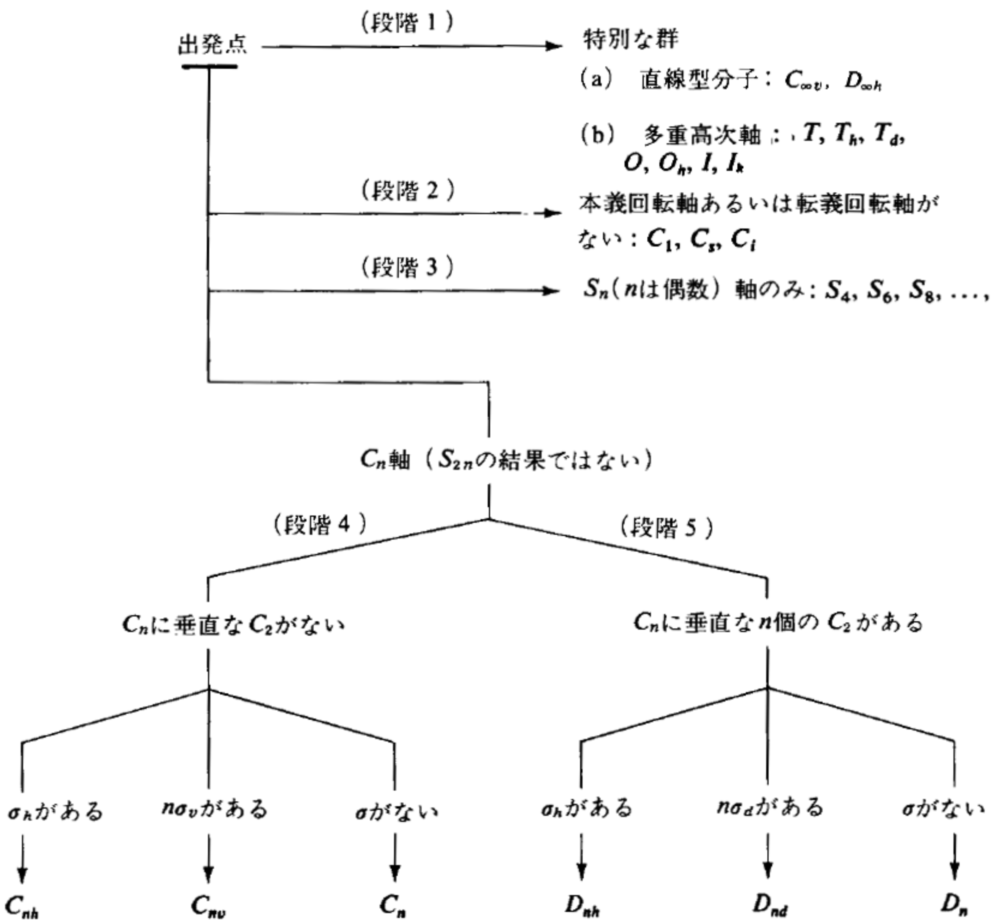
<u>How to determine the point group ?</u>

1. Determine if the molecule is of high or low symmetry.
2. If not, find the highest order rotation axis, C_n.
3. Determine if the molecule has any C_2 axes perpendicular to the principal C_n axis. If so, then there are n such C_2 axes, and the molecule is in the D set of point groups. If not, it is in either the C or S set of point groups.
4. Determine if the molecule has a horizontal mirror plane (σ_h) perpendicular to the principal C_n axis. If so, the molecule is either in the C_{nh} or D_{nh} set of point groups.
5. Determine if the molecule has a vertical mirror plane (σ_v) containing the principal C_n axis. If so, the molecule is either in the C_{nv} or D_{nd} set of point groups. If not, and if the molecule has n perpendicular C_2 axes, then it is part of the D_n set of point groups.
6. Determine if there is an improper rotation axis, S_{2n}, collinear with the principal C_n axis. If so, the molecule is in the S_{2n} point group. If not, the molecule is in the C_n point group.

Point Group Decision Tree



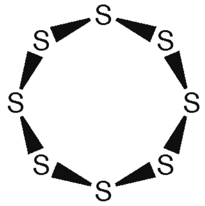
https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/symmetry/symmtry.htm



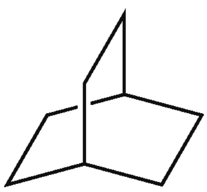
F.A. Cotton “Chemical Applications of Group Theory” 2nd Ed. 1971. (訳書は丸善)

Homework

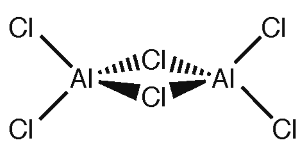
Answer the point group symbol of each compound.



(a)



(b)



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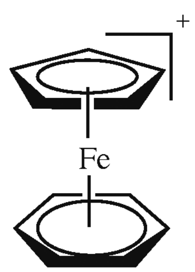

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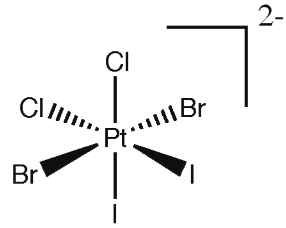


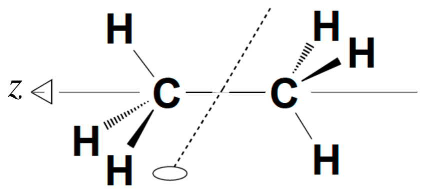
(e)

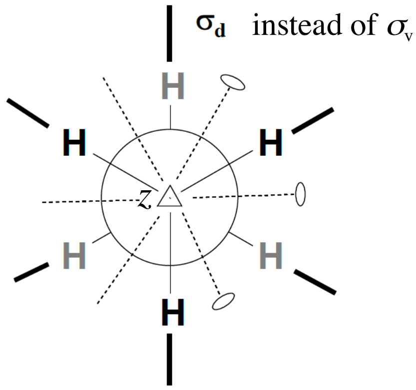
Appendix

Why we name σ_d instead of σ_v in a series of D point groups?

Ans.) When a mirro plane is found in a vertical direction (usually n σ_v) and in a direction just bisecting any two neiboring C_2'(xy) axes, the mirror plane is named a dihedral mirror plane, σ_d. The point group is named D_{nd}.

D_n群の要素を持ち，かつ全ての隣接したC_2軸の間の角を2等分する垂直なn個の鏡面（σ_d面）を持つ分子はD_{nd}点群に属す





Staggered configuration

C_2H_6 **D_{3d}**

Triangular antiprism