Symmetry and Group Theory – Exercise Set 3, Solutions

3.1) Show that all molecules are chiral that do not possess an S_n axis.

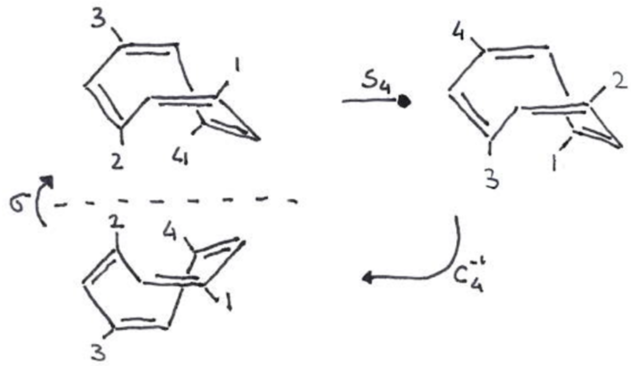
We can easily show that all molecules with an S_n axis are achiral.

$$C_n^{-1} S_n = C_n^{-1} C_n \sigma = \sigma$$

In other words, if one performs an S_n rotation followed by a C_n^{-1} rotation, one obtains the mirror image of the original configuration. That means that the molecule and its mirror image are superimposable. Hence, the molecule is achiral.
Since the only two symmetry elements are C_n and S_n axes (with $\sigma = S_1$ and $i = S_2$), all other molecules without S_n axes must be chiral.

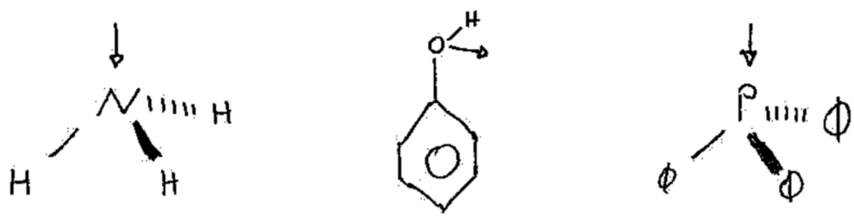
3.2) Determine the point group of 1,3,5,7-tetramethylcyclooctatetraene. Show that the molecule is achiral even though it does not have a reflection plane or a center of inversion.

Point group S_4.



3.3) Sketch the dipole moment in NH_3, phenol, PPh_3.

Note that we use the convention that the dipole points from the negative to the positive charge.



3.4) Show that the group multiplication table of $C_{2v} = \{E, C_2, \sigma_v(xz), \sigma_v(yz)\}$ is the one given below. Show this by expressing the symmetry operations by transformation matrices acting on a point in Cartesian coordinates $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
E	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
C_2	C_2	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

Filling out the first column and the top row is trivial, since $AE = EA = A$. Moreover, we have

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \sigma_v(xz) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \sigma_v(yz) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Clearly, for the C_{2v} point group, $A^2 = E$ for any element A, which explains the diagonal. Furthermore, we note that C_{2v} is Abelian. Therefore,

$$C_2\sigma_v(xz) = \sigma_v(xz)C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v(yz)$$

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$$\sigma_v(xz)\sigma_v(yz) = \sigma_v(yz)\sigma_v(xz) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = C_2$$

3.5) Show that $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$.

$$ABC[C^{-1}B^{-1}A^{-1}] = ABB^{-1}A^{-1} = \cdots = E$$

Therefore, $C^{-1}B^{-1}A^{-1}$ is the reciprocal of ABC, or $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$.

3.6) Are the natural numbers $\mathbb{N} = \{\mathbf{1}, \mathbf{2}, \mathbf{3}, \ldots\}$ a group with respect to multiplication?

1) Completeness: $n_1 \cdot n_2 = n_3$ ✔
2) Neutral element: $n \cdot E = n$, therefore $E = 1$ ✔
3) Associative law: $(n_1 n_2) n_3 = n_1 (n_2 n_3)$ ✔
4) Reciprocal element: $n \cdot n^{-1} = E = 1$, therfore $n^{-1} = \frac{1}{n}$, but $\frac{1}{n} \notin \mathbb{N}$ **X**

Because the last condition is not fulfilled, $\mathbb{N}$ does not form a group with respect to multiplication.

3.7) Are the integers $\mathbb{Z} = \{\ldots, -\mathbf{2}, -\mathbf{1}, \mathbf{0}, \mathbf{1}, \mathbf{2}, \ldots\}$ a group with respect to addition?

1) Completeness: $z_1 + z_2 = z_3$ ✔
2) Neutral element: $z + E = z$, therefore $E = 0$ ✔
3) Associative law: $(z_1 + z_2) + z_3 = z_1 + (z_2 + z_3)$ ✔
4) Reciprocal element: $z + z^{-1} = E = 0$, therfore $z^{-1} = -z$ ✔
5) Commutativity: $z_1 + z_2 = z_2 + z_1$ ✔

$\mathbb{Z}$ forms a group with respect to addition. Moreover, $\mathbb{Z}$ is Abelian.

3.8) Name subgroups of C_{2v}.

Subgroups of $C_{2v} = \{E, C_2, \sigma_v, \sigma_v'\}$ are $C_1 = \{E\}$, $C_s = \{E, \sigma_v\}$, and $C_2 = \{E, C_2\}$.

3.9) *A* , *B*, and *C* are elements of a group. Prove that if *A* is conjugate with *B* and *A* is conjugate with *C*, then *B* is conjugate with *C*.

Since $A = X^{-1}BX$ and $A = Y^{-1}CY$, it follows that

$$X^{-1}BX = Y^{-1}CY$$

By left-multiplying with X and right-multiplying with X^{-1}, we obtain

$$B = (XY^{-1})C(YX^{-1})$$

Since XY^{-1} must be another element of the group, say Z

$$XY^{-1} = Z$$

and $YX^{-1} = (XY^{-1})^{-1}$, we find

$$B = (XY^{-1})C(YX^{-1}) = ZCZ^{-1}$$

Therefore, B and C are conjugate.

3.10) Determine the multiplication table of the group G_3 = {E, A, B}. What can you tell about the properties of this group? Determine the classes of G_3.

It is easy to fill out the first column and row of the multiplication table.

G_3	E	A	B
E	E	A	B
A	A		
B	B		

In order to find the product $A \cdot A$, we consider the different possibilities. This becomes simple when we consider that in each row and column of a group multiplication table, each element must appear exactly once. (Prove that this is the case!)

If we choose $A \cdot A = E$, we would therefore get $B \cdot A = B$ in the second column, so that $A = E$. However, A has to be different from E.

Similarly, if we choose $A \cdot A = A$, this also leads to $A = E$.

This only leaves $A \cdot A = B$. Filling out the rest of the table is straightforward.

G_3	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

We can see that G_3 is cyclic and therefore Abelian.

Since G_3 is Abelian, $X^{-1}AX = X^{-1}XA = A$. Therefore, every element forms its own class.

Homework

3.11) Determine the point groups of the following molecules and objects.

A	C_{2v}
B	C_{3h}
C	C_1
D	$C_{\infty v}$
E	C_{2h}
F	D_{4d}
G	C_i
H	D_{2d}

3.12) Construct the group multiplication table of the point group C2h. Determine the classes of the point group C2h.

C_{2h}	E	C_2	i	σ_h
E	E	C_2	i	σ_h
C_2	C_2	E	σ_h	i
i	i	σ_h	E	C_2
σ_h	σ_h	i	C_2	E

The point group C_{2h} is Abelian (multiplication table symmetric with respect to the diagonal). Since all the elements commute, every element is only conjugate with itself. The classes of C_{2h} therefore are $\{E\}$, $\{C_2\}$, $\{i\}$, $\{\sigma_h\}$.

3.13) Which point group is obtained if one deletes the inversion operation i from the point group S6?

If we lower the symmetry of a molecule, its new point group must be a subgroup of its original point group. The subgroups of S_6 are C_1, C_i, and C_3. Since the new point group does not have a center of inversion, it must be either C_1 or C_3. Since we did not delete any operation associated with the C_3 axis, the new point group must be C_3.

3.14) Show that the numbers $\{c, c^2, c^3, \dots, c^n\}$ with $c = e^{i\frac{2\pi}{n}}$ and integer n form a group with respect to multiplication.

1) Completeness, any product $c^p c^q = c^{p+q}$ is another element of the group since $p + q$ is another integer and since $e^{i\frac{2\pi}{n}+i2\pi k} = e^{i\frac{2\pi}{n}}$ for any $k \in \mathbb{Z}$.
2) Existence of a neutral element, $E = c^n = 1$ and 1 is the neutral element for multiplication of complex numbers.
3) Multiplication of complex numbers is associative.
4) Every element has a reciprocal, $(c^p)^{-1} = c^{-p} = c^{n-p}$.

The point group C_n is cyclic, generated by the rotation C_n. The isomorphism Γ: $C_n \to \{c, c^2, \dots, c^n\}$, $\Gamma(C_n^k) = c_n^k$, is a 1-dimensional representation of the point group C_n.

3.15) Show that $\boldsymbol{G = \{1, -1, i, -i\}}$ is a group with respect to multiplication. Here, *i* refers to the complex number with $\boldsymbol{i^2 = -1}$.

a) First, write down the group multiplication table.
b) Then show that G meets all the criteria for the definition of a group.
c) Which special properties does the group G have?

a)

G	1	i	-1	-i
1	1	i	-1	-i
i	i	-1	-i	1
-1	-1	-i	1	i
-i	-i	1	i	-1

b)

1) Completeness as demonstrated by the group multiplication table
2) Existence of a neutral element, $E = 1$
3) Multiplication of complex numbers is associative.
4) Every element has a reciprocal, $(1)^{-1} = 1$, $(i)^{-1} = -i$, $(-1)^{-1} = -1$, $(-i)^{-1} = i$

c) The group is cyclic (all elements are powers of i) and therefore also Abelian.

The point group C_4 is cyclic, generated by the rotation C_4. The isomorphism Γ: $C_4 \to \{1, -1, i, -i\}$, $\Gamma(C_4^k) = i^k$, is a 1-dimensional representation of the point group C_4. (That can also be obtained from exercise 3.14, by taking $n = 4$, in which case $c = i$.)