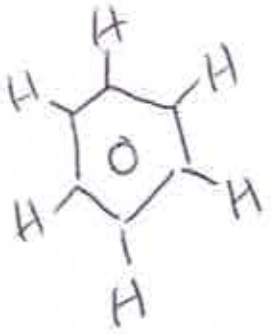
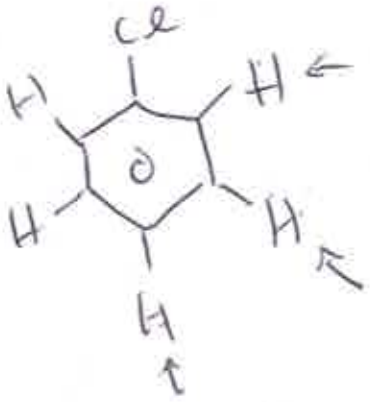
9/6/16 Lecture 04 CH431

^{1}H NMR of



benzene



chlorobenzene

1 unique proton

3 unique protons

→ different symmetry → different ^{1}H NMR spectra

Symmetry

Names: _____

_____

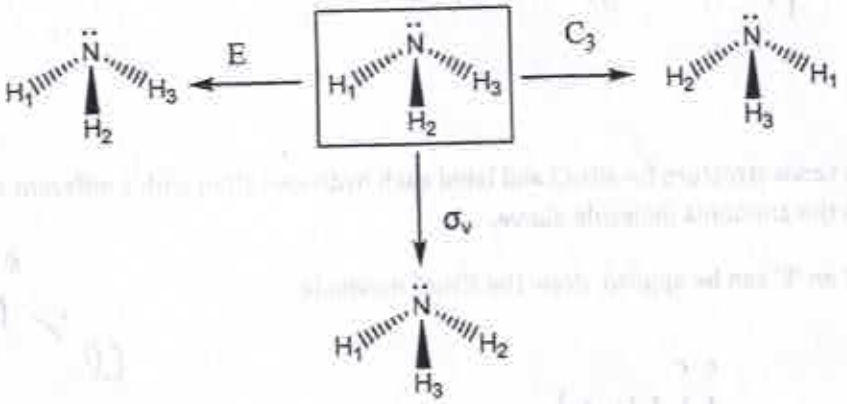
_____

_____

Model 1: Ammonia

In groups, consider the three dimensional ammonia molecule in the box below. You may find it useful to use a model kit to build one or more molecules. (Hint: It will be easier to see changes in position of atoms if all H atoms are not the same color.) For each question you must agree on the answer before moving to the next question.

trigonal pyramidal (tetrahedral) w/ one lone pair



Critical Thinking Questions

1. How does the ammonia molecule in the box change when 'E' is applied?

nothing , 360° rotation

2. How does the ammonia molecule in the box change when 'C_3' is applied? (Hint: What does the 3 tell us?)

rotation, you can do 3 rotations to get to original configuration

3. How does the ammonia molecule in the box change when 'σ_v' is applied?

σ_v = "sigma" v

H_3 & H_2 switch places

reflection across H^* bond

120° rotation

$\downarrow$

$\frac{360^\circ}{3}$

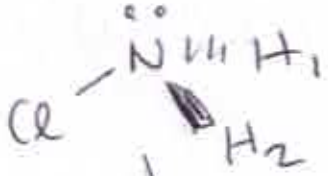
$n \rightarrow 3$

4. When a 'σ_v' is applied to the molecule, the structure of the molecule before 'σ_v' is identical to the structure of the molecule after 'σ_v'. Draw the other two possible results when 'σ_v' is applied to the ammonia molecule in the box. The 'σ_v' is also called a 'mirror plane'. How many such mirror planes are there in ammonia? (Hint: Use a model kit to help you see changes in the positions of atoms.)

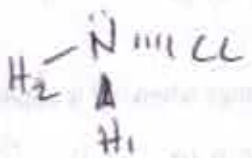
3 σ_v ; one along each N-H bond

5. Draw the Lewis structure for NH_2Cl and label each hydrogen atom with a different subscript similar to the ammonia molecule above.

   a. If an 'E' can be applied, draw the NH_2Cl molecule.

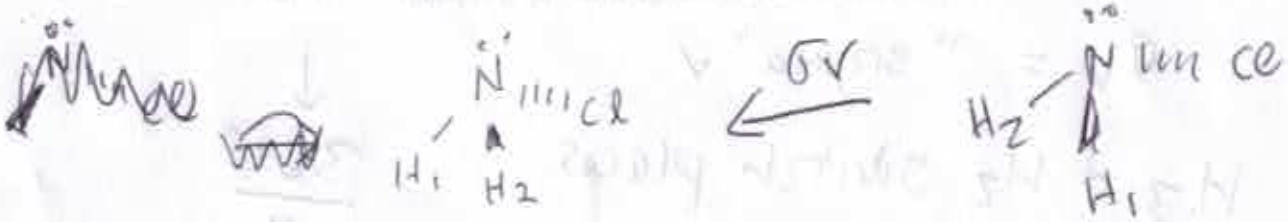


   b. If a 'C_3' can be applied, draw the NH_2Cl molecule.



no C_3 in NH_2Cl

   c. If a 'σ_v' can be applied, draw the NH_2Cl molecule.



Information

All molecules can be described in terms of symmetry. Here are several different statements to describe what is meant by 'symmetry operation'.

A symmetry operation is a movement of a body such that after the movement has been carried out every point of the body looks like it is in its original position.

If you close your eyes when the symmetry operation is performed, and, if you cannot tell that the operation has occurred after you open your eyes, then it was a valid symmetry operation.

"A symmetry element is a geometrical entity such as a line, plane or point that can be used to carry out a symmetry operation." (Cotton, 1971).

In order for the operation to be considered symmetrical, the position and orientation of the atoms relative to one another within the molecule must be the same after the operation as it was before the operation.

Critical Thinking Questions

6. Identity Symmetry Operation:

   a. Define the identity symmetry operation, 'E'. (Everyone in the group must agree.)

   Do nothing to molecule

   b. Will all molecules have the identity symmetry operation, 'E'? Explain.

   Yes

7. Rotation symmetry operation:

   a. Define the rotation symmetry operation, 'C_3'.

   rotation by $\frac{360}{3} = 120^\circ$

   3 C_3 rotatio

   ↓

   $C_3^3 = E$

   b. Will all molecules have the rotation symmetry operation, 'C_3'? Explain.

   no

c. What does the 3 in 'C_3' tell us about the rotation symmetry operation?

$360/3 = 120°$ rotation, $C_3^3 = E$

8. Reflection symmetry operation:

a. Define the reflection symmetry operation, 'σ_v'.

mirror reflection

vertical plane; along one of the bonds

b. Will all the molecules have the reflection symmetry operation, 'σ_v'? Explain.

NO

9. Given your definition of a C_3 symmetry operation, would you answer question 5b any differently now? If yes, how?

NH_2Cl does not have a C_3

References

Cotton, Albert F. *Chemical Applications of Group Theory*, 2nd Ed. John Wiley & Sons: New York, 1971.