Objective

After completing this section, you should be able to apply the concept of hybridization of atoms such as N, O, P and S to explain the structures of simple species containing these atoms.

Key Terms

Make certain that you can define, and use in context, the key term below.

- lone pair electrons

Study Notes

Nitrogen is frequently found in organic compounds. As with carbon atoms, nitrogen atoms can be $sp^3$, $sp^2$- or $sp$-hybridized.

Note that, in this course, the term "lone pair" is used to describe an unshared pair of electrons.

The valence-bond concept of orbital hybridization can be extrapolated to other atoms including nitrogen, oxygen, phosphorus, and sulfur. In other compounds, covalent bonds that are formed can be described using hybrid orbitals.

The nitrogen is $sp^3$ hybridized which means that it has four $sp^3$ hybrid orbitals. Two of the $sp^3$ hybridized orbitals overlap with s orbitals from hydrogens to form the two N-H sigma bonds. One of the $sp^3$ hybridized orbitals overlap with an $sp^3$ hybridized orbital from carbon to form the C-N sigma bond. The lone pair electrons on the nitrogen are contained in the last $sp^3$ hybridized orbital. Due to the $sp^3$ hybridization the nitrogen has a tetrahedral geometry. However, the H-N-H and H-N-C bonds angles are less than the typical 109.5° due to compression by the lone pair electrons.

\[
\begin{align*}
\text{Methylamine} \\
\begin{array}{c}
\text{N} \\
\text{H} & \text{CH}_3
\end{array}
\end{align*}
\]

The oxygen is $sp^3$ hybridized which means that it has four $sp^3$ hybrid orbitals. One of the $sp^3$ hybridized orbitals overlap with s orbitals from a hydrogen to form the O-H sigma bonds. One of the $sp^3$ hybridized orbitals overlap with an $sp^3$ hybridized orbital from carbon to form the C-O sigma bond. Both the sets of lone pair electrons on the oxygen are contained in the remaining $sp^3$ hybridized orbital. Due to the $sp^3$ hybridization the oxygen has a tetrahedral geometry. However, the H-O-C bond angles are less than the typical 109.5° due to compression by the lone pair electrons.
Phosphorus can have expanded octets because it is in the n = 3 row. Typically, phosphorus forms five covalent bonds. In biological molecules, phosphorus is usually found in organophosphates. Organophosphates are made up of a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to a carbon. In methyl phosphate, the phosphorus is \( sp^3 \) hybridized and the O-P-O bond angle varies from 110° to 112°.

In biological systems, sulfur is typically found in molecules called thiols or sulfides. In a thiol, the sulfur atom is bonded to one hydrogen and one carbon and is analogous to an alcohol O-H bond. In a sulfide, the sulfur is bonded to two carbons. In both cases the sulfur is \( sp^3 \) hybridized and the bond angles are much less than the typical 109.5°.
Questions

Q1.10.1

Identify geometry and lone pairs on each heteroatom of the molecules given.

\[ \text{Diethyl Ether} \quad \text{Dimethylamine} \]

Solutions

S1.10.1

Diethyl ether would have two lone pairs of electrons and would have a bent geometry around the oxygen.

Dimethyl amine would have one lone pair and would show a pyramidal geometry around the nitrogen.

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)