

- b. Adding an electron to O_3 decreases the angle, as the odd electron spends part of its time on the central O, making two positions for electron repulsion. The decrease in angle is small, however, with angles of 113.0 to 114.6 pm reported for alkali metal ozonides (see W. Klein, K. Armbruster, M. Jansen, *Chem. Commun.*, **1998**, 707) in comparison with 116.8° for ozone.

3.14

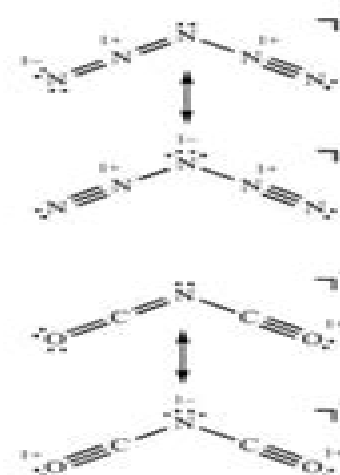


As the groups attached to oxygen become less electronegative, the oxygen atom is better able to attract shared electrons to itself, increasing the *bp-bp* repulsions and increasing the bond angle. In the case of $O(SiH_3)_2$, the very large increase in bond angle over $O(CH_3)_2$ suggests that the size of the SiH_3 group also has a significant effect on the bond angle.

3.15

C_3O_2 has the linear structure $O=C-C-C=O$, with zero formal charges.

N_5^+ with the same electronic structure has formal charges of 1-, 1+, 1+, 1+, 1-, unlikely because three positive charges are adjacent to each other. Changing to $N=N=N-N=N$ results in formal charges of 1-, 1+, 0, 1+, 0, a more reasonable result with an approximately trigonal angle in the middle. With triple bonds on each end, the formal charges are 0, 1+, 1-, 1+, 0 and a tetrahedral angle. Some contribution from this would reduce the bond angle.



$OCNCO^+$ can have the structure $O=C-N-C=O$, with formal charges of 1+, 0, 1-, 0, 1+ and two lone pairs on the central N. This would result in an even smaller angle in the middle, but has positive formal charges on O, the most electronegative atom. $O=C=N-C=O$ has a formal charge of 1+ on the final O. Resonance would reduce that formal charge, making this structure and a trigonal angle more likely. The Seppelt reference also mentions two lone pairs on N and cites "the markedly higher electronegativity of the nitrogen atom with respect to the central atom in C_3O_2 , which leads to a higher localization of electron density in the sense of a nonbonding electron pair." Therefore, the bond angles should be $OCNCO^+ > OCNCO^+ > N_5^+$. Literature values are 180°, 130.7°, and 108.3 to 112.3° (calculated), respectively.

3.16

a.



In ethylene, carbon has *p* orbitals not involved in sigma bonding. These orbitals interact to form a pi bond between the carbons, resulting in planar geometry. (Sigma and pi

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1. Understanding the eBook Chemistry Chapter 14 Solutions Manual
 - The Rise of Digital Reading Chemistry Chapter 14 Solutions Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Chemistry Chapter 14 Solutions Manual
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Chemistry Chapter 14 Solutions Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Chemistry Chapter 14 Solutions Manual

-
- Personalized Recommendations
 - Chemistry Chapter 14 Solutions Manual User Reviews and Ratings
 - Chemistry Chapter 14 Solutions Manual and Bestseller Lists
5. Accessing Chemistry Chapter 14 Solutions Manual Free and Paid eBooks
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 - Interactive Elements Chemistry Chapter 14 Solutions Manual
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 - Creating a Diverse Reading Collection Chemistry Chapter 14 Solutions Manual
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 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Chemistry Chapter 14 Solutions Manual
 - Setting Reading Goals Chemistry Chapter 14 Solutions Manual
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Chemistry Chapter 14 Solutions Manual

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- Distinguishing Credible Sources

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- Utilizing eBooks for Skill Development
- Exploring Educational eBooks

14. Embracing eBook Trends

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- Interactive and Gamified eBooks

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