Bond Order and Chemical Properties of BF, CO, and N₂

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Supporting Information

ABSTRACT: The traditional chemical approaches, Lewis electron dot structures and molecular orbital theory, predict the relative bond orders of boron monofluoride, carbon monoxide, and dinitrogen to be BF < CO < N₂. This is quantified by quantum mechanical, theoretical studies that show the bond orders to be ~1.4, ~2.6, and ~3.0, respectively. These results also confirm the chemical intuition that the change in bond order is primarily due to the π component. The differences in bond order have a dramatic effect on the ligand behavior of the three molecules, particularly the propensity of BF to function as a bridging ligand.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Physical Chemistry, Misconceptions/Discrepant Events, Textbooks/Reference Books, Covalent Bonding, Lewis Structures, MO Theory, Main-Group Elements, Organometallics

Students are introduced to N₂ and CO in general chemistry, and their prominence continues in inorganic chemistry and physical chemistry. However, their isoelectronic relative, BF, is much less considered. Together, this trio of diatomic molecules comprises a series that superbly exemplifies numerous bonding and chemical trends. The changes in bonding lead to three molecules that behave very differently, especially as ligands, with BF appearing only recently in the chemical literature as a bridging ligand. In this work, this series of molecules is used to compare the predictions of various chemical models, including Lewis bonding concepts, simple molecular orbital theory, and computational methods. We then relate the predictions of these models to ligand behavior.

TRADITIONAL APPROACH

The contrasting behaviors of these molecules result from the differences in their bonding. A first look at the chemical bonding of BF, CO, and N₂ is provided by their respective Lewis structures (Figure 1). The creation of accurate Lewis structures is a balance between minimizing the formal charge and completing the octet. In N₂, both these properties can be obtained without compromise. 1. For CO, there is one structure that completes the octets, 2, whereas another minimizes the formal charge, 3. BF is similar, but with three structures in competition, 4, 5, and 6. The triple-bonded structure, 4, though it fits the pattern of its isoelectronic relatives, is not a formally correct structure because it has formal charges greater than ±1, in violation of the Pauling electroneutrality principle. Structures 5 and 6 are preferred for BF even though they do not have a complete octet for boron, as this is not uncommon in boron chemistry. When two structures are valid for a given molecule, both are considered to contribute to a resonance hybrid. Therefore, on the basis of Lewis ideas, the bond order of N₂ is predicted to be 3; CO between 2 and 3; and BF between 1 and 2.

Though Lewis structures are valuable as a simple tool, molecular orbital (MO) theory is a more nuanced approach, which, among other insights, distinguishes between σ and π antibonding and bonding orbitals. A basic principle of MO theory is that when the atomic orbitals are more disparate in energy, the interaction will be weaker and the resulting molecular orbital will be composed of greater character from the atomic orbital closest in energy. Furthermore, because orbital energies become more negative with increasing electronegativity (χ), the greater the electronegativity difference, the greater the difference in orbital energy.

The essential difference between these three isoelectronic diatomic molecules is the electronegativity difference (Δχ) between the two constituent atoms. Obviously, in N₂, Δχ is zero and the electrons are equally shared. In contrast, the Δχ of CO and BF is 0.89 and 1.94, respectively (by the Pauling scale). The extent to which the molecular orbitals are affected by Δχ is different for the σ and π orbitals in these diatomic molecules. For the π molecular orbitals, the constituent p atomic orbitals are further apart in energy with increasing Δχ; the bonding interaction is therefore weaker, and the molecular orbital is ultimately composed of more character from the more electronegative atom (Figure 2). This results in a molecular orbital that is spatially located toward the more electronegative atom and increasingly resembles a nonbonding (nb) orbital rather than a bonding orbital (Figure 3).

The effect of Δχ on the σ orbitals is different because the bonding picture is more complicated. Both the s and pσ atomic orbitals are involved, and whereas pσ orbitals decrease in energy with increasing electronegativity, s orbitals do so even more. As a result, the 2pσ orbital of the more electronegative atom...
approaches the 2s orbital of the less electronegative atom, which is energetically isolated from its counterpart on the more electronegative atom to form a strong $\sigma$ interaction (Figure 4). Therefore, the $\sigma$ orbitals possess significant orbital character from the 2s orbital of the less electronegative atom and consequently these orbitals tend to maintain their bonding character even as $\Delta \chi$ increases.

With less $\pi$ bonding due to electronegativity perturbation, the $\pi$ bond orders are expected to follow the pattern: BF $<$ CO $<$ N$_2$. Since the $\sigma$ orbitals are less affected, the $\sigma$ bond orders ought to be fairly invariant through the series, and therefore, the overall bond orders are expected to follow the pattern of the $\pi$ bond orders. We now check these qualitative statements with computational studies, and thereby provide numerical support for these conjectures. For additional details, see the Supporting Information.

### COMPUTATIONAL SUPPORT

Traditional chemical models reveal interesting differences in the bonding of BF, CO, and N$_2$, and by extension, their chemical properties. However, the argument can be made more robust with the addition of a quantum-mechanical approach through computational experiments. We discuss the overall bond orders, $\sigma$ bond strengths, and $\pi$ bond strengths. Figure 5 depicts the bond orders for each of the three molecules, which were calculated using ADF (Amsterdam Density Functional software). The Gopinathan–Jug bond index was used here, as it is superior to the Mayer method previously described in this Journal, because of the latter’s high basis set dependence. (For more information on how the calculations were run and results obtained, see the Supporting Information.) Note that bond order is not an observable chemical property, but...
A REPRiSE ON BF

The bonding in BF has previously been commented upon in this Journal.25 Experimental bond lengths in B—N, B—O, and B—F compounds were employed to infer relative bond orders. On the basis of the experimental bond length of 1.263 Å,26 Straub asserted that BF has a triple bond. However, we disagree that just because it is on the shorter end of known B—F bond lengths, that it therefore has a bond order of three. It is in fact only in the second quartile of the full range of B—F bond lengths listed in the article25 (1.21—1.40 Å). Our computational bond length of 1.281 Å and dipole moment of 0.97 D are both in substantial agreement with the experimental results. The Pauling electroneutrality principle, the contrasting perturbations of the σ and π molecular orbitals, and the computed bond orders and bond energies based upon the electron density distribution all point to a bond order substantially less than three.

CONCLUSION

The traditional chemical approaches, Lewis electron dot structures and molecular orbital theory, predict the relative bond orders to be BF < CO < N2. This is quantified by quantum-mechanical calculations that show the bond orders to be ~1.4, ~2.6, and ~3.0, respectively. These theoretical studies also confirm the chemical intuition that the change in bond order is mainly due to the π component. Furthermore, the differences in bond order have a dramatic effect on the ligand behavior of BF compared to CO and N2.

ASSOCIATED CONTENT

5 Supporting Information
Additional discussion of molecular orbital interactions; details of the computational software and its implementation; a more detailed table of results. This material is available via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Ryan Martinie acknowledges the support of a grant from the Calvin College Integrated Science Research Institute, funded by the Howard Hughes Medical Institute. We gratefully acknowledge the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. Computer hardware was provided by a Major Research Instrumentation Grant from the National Science Foundation, Award No. OCI-0722819.
REFERENCES


(12) In contrast, the LUMO π* orbital is located primarily on the less electronegative atom, making BF more suited for π backbonding than CO and N₂.


(20) The reader may observe that the sum of the sigma and pi bond strengths are 715, 693, and 446 kcal/mol for N₂, CO, and BF, respectively. Whereas, the experimental bond dissociation energies are much less: ~230, ~255, and ~180 kcal/mol, respectively. The difference is due to the Pauli repulsion and the electrostatic interaction between the atomic reference states for these three systems. See the article by Frenking for details. Furthermore, Frenking discusses two sets of reference atomic states for CO. We have adopted only one of those two in our discussion.


(22) The basis for this theoretical study is found in the work of M. Cowie and co-workers, for example, 23.


(24) All calculations were completed with the Gaussian03 suite of programs at B3LYP/cc-pVTZ on C, H, O, and P and LANL2DZ for Ir and Ru. Frisch, M. J. et al. Gaussian 03, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2003.
