

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

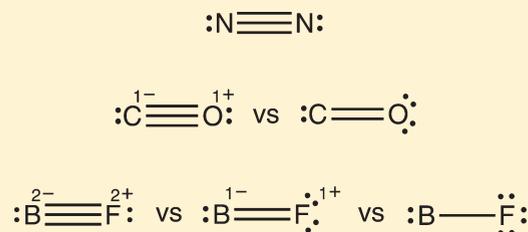
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 Supporting Information

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 $\text{BF} < \text{CO} < \text{N}_2$. 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^{1–3} and physical chemistry.⁴ 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.^{5–7} 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.⁸ 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.² 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.^{9,10} 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.¹¹ Furthermore, because orbital energies become more negative with increasing electronegativity χ ,^{9,11} the greater the electronegativity difference, the greater the difference in atomic orbital energy.

The essential difference between these three isoelectronic diatomic molecules is the electronegativity difference ($\Delta\chi$) between the two constituent atoms. Obviously, in N₂, $\Delta\chi$ is zero and the electrons are equally shared. In contrast, the $\Delta\chi$ 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 $\Delta\chi$ 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 $\Delta\chi$; 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).¹²

The effect of $\Delta\chi$ on the σ orbitals is different because the bonding picture is more complicated. Both the s and p_z atomic orbitals are involved, and whereas p orbitals decrease in energy with increasing electronegativity, s orbitals do so even more.⁹ As a result, the 2p_z orbital of the more electronegative atom

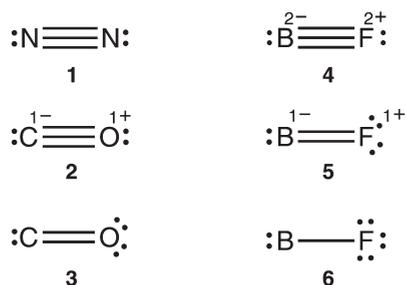


Figure 1. Lewis structures of BF, CO, and N₂.

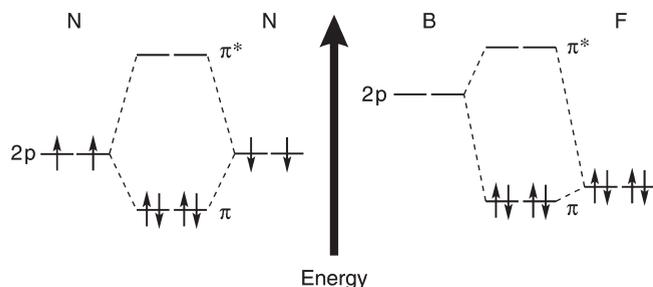


Figure 2. Molecular orbital diagram for N₂ and BF (π orbitals only).

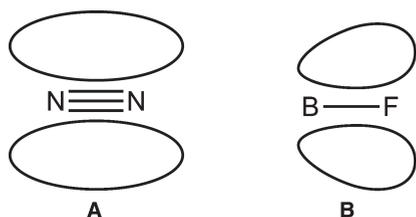


Figure 3. Depictions of π bonding orbitals in (A) N₂ and (B) BF. Detailed orbital contour diagrams are presented in the Supporting Information.

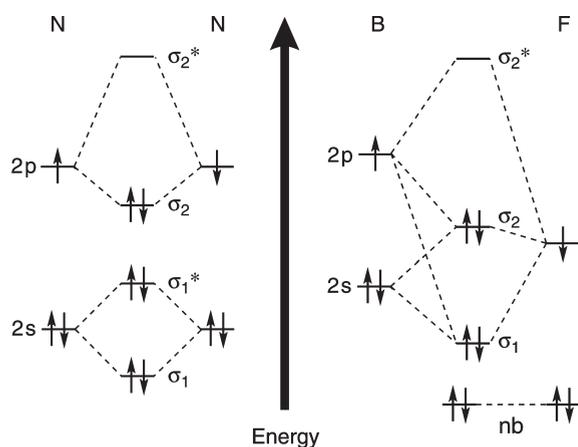


Figure 4. Molecular orbital diagrams for N₂ and BF (σ orbitals only).

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 σ interaction (Figure 4). Therefore, the σ orbitals possess significant orbital character

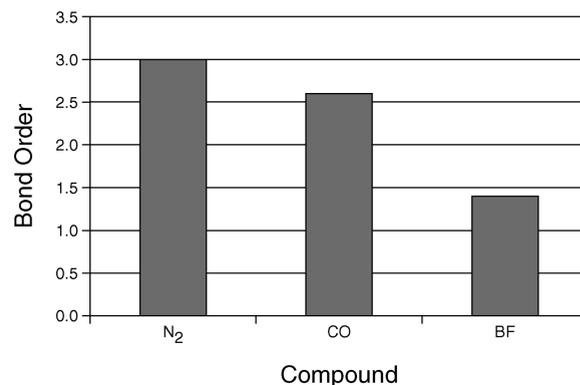


Figure 5. Calculated bond orders of N₂, CO, and BF.

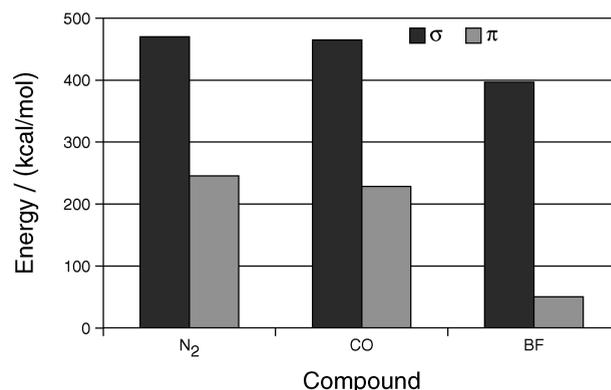


Figure 6. Orbital interaction strengths (σ and π) for N₂, CO, and BF.

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 π bonding due to electronegativity perturbation, the π bond orders are expected to follow the pattern: BF < CO < N₂. Since the σ orbitals are less affected by the series, and therefore, the overall bond orders are expected to follow the pattern of the π 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 N₂, 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, σ bond strengths, and π bond strengths. Figure 5 depicts the bond orders for each of the three molecules, which were calculated using ADF (Amsterdam Density Functional software).^{13,14} The Gopinathan–Jug^{15,16} bond index was used here, as it is superior to the Mayer method previously described in this Journal,¹⁷ because of the latter's high basis set dependence.¹⁸ (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

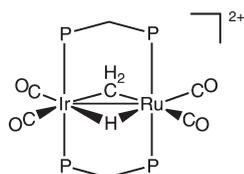


Figure 7. $[\text{IrRu}(\text{CO})_4(\mu\text{-CH}_2)(\mu\text{-H})(\text{H}_2\text{PCH}_2\text{PH}_2)_2]$, a methylene bridged complex.

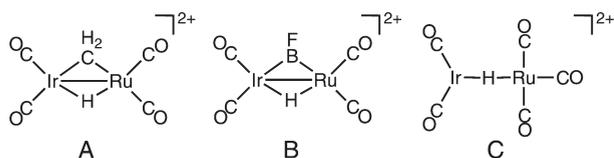


Figure 8. (A) Original CH_2 structure, (B) BF substitution, and (C) CO substitution. Top-down view. dhpmp ligands not depicted.

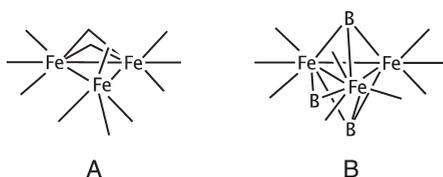


Figure 9. Trinuclear iron complex with 12 isoelectronic ligands (A) no BF: $\text{Fe}_3(\text{CO})_{10}(\mu_2\text{-CO})_2$ and (B) three BF ligands: $\text{Fe}_3(\text{CO})_9(\mu_2\text{-BF})(\mu_3\text{-BF})_2$.

rather a tool for better understanding electronic interactions. As can be seen, the calculated bond orders strongly corroborate the traditional chemical approach outlined above, with calculated orders of 3.0, 2.6, and 1.4 for N_2 , CO, and BF, respectively.

Figure 6 shows the σ bond and π bond strengths.¹⁹ As expected, the σ bond strengths are similar across the series, decreasing only 16%, whereas the π bonding in BF is significantly weaker than N_2 and CO, decreasing by about 80%. Clearly, the decrease in bond order in BF is due mainly to a loss in π bonding.²⁰

APPLICATION

Having examined the bonding differences in N_2 , CO, and BF, we now turn to how these differences affect their chemical properties. We focus on the differences in ligand properties. N_2 can be an end-on or side-on ligand with a host of midtransition metals,²¹ but not to the extent of CO, which is ubiquitous and flexible as a ligand in inorganic chemistry.¹ Because the HOMO is located predominantly on the carbon atom, CO readily functions as a Lewis base and end-on ligand.⁹ Furthermore, Lewis structure 3 (Figure 1) can be rewritten such that each electron of the lone pair on the carbon atom occupies a separate orbital, allowing the CO ligand to bridge two metal atoms. For CO to bridge three metal atoms is not as common.^{1,10} BF, though a relatively uncommon ligand, also readily bridges metal atoms and is energetically preferred over CO for bridging three metal atoms.^{6,7} This relates to the lower bond order; having only a single bond allows BF to form more bonds to the metal atoms.

To explore this idea, we have computationally examined binuclear transition-metal complexes with various bridging ligands.²² The complex $[\text{IrRu}(\text{CO})_4(\mu\text{-CH}_2)(\mu\text{-H})(\text{dhpmp})_2]$

(dhpmp = $\text{H}_2\text{PCH}_2\text{PH}_2$) (Figure 7) has a bridging methylene and a bridging hydride, but the system gives an ideal opportunity to compare the propensity for bridging of CO and BF. Both ligands can be isolobal to CH_2 ,¹¹ and by replacing the $\mu\text{-CH}_2$ with CO and BF, respectively, the bridging propensities can be theoretically compared. The resulting geometries suggest that BF energetically favors a bridging position over CO (Figure 8).²⁴

Another example can be found in the chemical literature.^{6,7} In the tri-iron cluster when three CO ligands are replaced with BF ligands, two of the BF ligands are triply bridging (μ_3) and one is edge-bridging (μ_2) (Figure 9).

A REPRIS 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 $\text{BF} < \text{CO} < \text{N}_2$. 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 N_2 .

ASSOCIATED CONTENT

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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REFERENCES

- (1) Cotton, F. A.; Wilkinson, G. Transition Metal Carbon Monoxide Compounds. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; 1021–1051. A later edition of this text has been published, but does not include this chapter.
- (2) Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*, 3rd ed.; Prentice Hall: New York, 2007; 376–489 and 325–375.
- (3) Radius, U.; Bickelhaupt, F. M.; Ehlers, A. W.; Goldberg, N.; Hoffmann, R. *Inorg. Chem.* **1998**, *37*, 1080–1090.
- (4) Atkins, P.; De Paula, J. *Physical Chemistry*, 8th ed.; W. H. Freeman and Company: New York, 2006; 373–384.
- (5) Vidovic, D.; Aldridge, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 3669.
- (6) Xu, L.; Li, Q.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2010**, *49*, 1046–1055 and references therein.
- (7) Xu, L.; Li, Q.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2010**, *49*, 2996–3001 and references therein.
- (8) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; 172–174.
- (9) DeKock, R. L.; Gray, H. B. *Chemical Structure and Bonding*; University Science Books: Sausalito, CA, 1989.
- (10) Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 4th ed.; Prentice Hall: New York, 2010; 126–168.
- (11) Albright, T. A.; Burdett, J. K.; Whangbo, M. Concepts of Bonding and Orbital Interaction. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; 12–25.
- (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.
- (13) te Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Gisbergen, S. J. A. V.; Snijders, J. G.; Ziegler, T. J. *Comput. Chem.* **2001**, *22*, 931–967.
- (14) ADF2009.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.
- (15) Gopinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *63*, 497–509.
- (16) Ponec, R.; Uhlik, F.; Cooper, D. L.; Jug, K. *Croat. Chem. Acta* **1996**, *69*, 933–940.
- (17) Sannigrahi, A. B.; Kar, T. J. *Chem. Educ.* **1988**, *65*, 674.
- (18) Michalak, A.; DeKock, R. L.; Ziegler, T. J. *Phys. Chem. A* **2008**, *112*, 7256–7263.
- (19) Esterhuysen, C.; Frenking, G. *Theor. Chem. Acc.* **2004**, *111*, 381–389.
- (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.¹⁹ Furthermore, Frenking discusses two sets of reference atomic states for CO. We have adopted only one of those two in our discussion.
- (21) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*–202, 379–409.
- (22) The basis for this theoretical study is found in the work of M. Cowie and co-workers, for example, 23.
- (23) Samant, R. G.; Trepanier, S. J.; Wigginton, J. R.; Xu, L.; Bierenstiel, M.; McDonald, R.; Ferguson, M. J.; Cowie, M. *Organometallics* **2009**, *28*, 3407–3420.
- (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.
- (25) Straub, D. K. *J. Chem. Educ.* **1995**, *72*, 494.
- (26) Cazzoli, G.; Cludi, L.; Degli Esposti, C.; Dore, L. *J. Mol. Spectrosc.* **1989**, *134*, 159–167.