Correspondence

Bernstein's Bond Length–Bond Order Relationship As Applied to C–N, C–O, and N–O Bonds in Metal Complexes

Sir:

Cotton and Wilkinson[1] have carefully outlined the qualitative relationships which exist between the bond properties length, dissociation energy, and force constant and their correlation with the bond order. As they indicate, linearity is not to be expected in a plot of any one bond parameter against any other over an appreciable range of values. Yet without linearity, quantitative relationships of empirical origin,[2] such as the one presented by Cotton and Wing, are little used.

At the risk of being redundant, we wish to point out that Bernstein[3] developed an interesting model which allows a simple quantitative relationship between bond order and bond length to be achieved. To quote Bernstein's 1947 article, "it would not seem worthwhile to propose yet another relation of this nature unless it succeeded in simplifying the present position of the problem."

The Bernstein model assumes that the tetrahedral angle is well preserved in compounds with single, double, and triple bonds. An *ad hoc* model for an M═M double bond arises by assuming two normal single bonds bent in circles while the tetrahedral angle is maintained, *i.e.*, tetrahedra are edge joined. Similarly the M≡M triple bond requires three "circular" bent bonds between "face-joined" tetrahedra. This model leads to

$$R_{\mathrm{M-M}} = \frac{2}{3}R^{\mathrm{S}}{}_{\mathrm{M-M}} + \frac{1}{3}R^{\mathrm{S}}{}_{\mathrm{M-M}}\left(\frac{1}{3}\right)^{P/2} \qquad (1)$$

where $R_{\mathrm{M-M}}$ is the distance for bond order $(P + 1)$ and $R^{\mathrm{S}}{}_{\mathrm{M-M}}$ is the single-bond M–M distance. Bernstein generalized the relationship to fit the form of a known empirical expression involving the principal quantum number *n*. Experimentally, however, this generalization seems unjustified. Besides, it might be argued that the tetrahedral model should work only when d- and f-orbital contributions are negligible, that is, when sp^3 hybridization is dominant. Lack of d- or f-orbital complications may be the reason the model works so well only with first-row elements, boron through fluorine.

By putting eq 1 in a different form and taking logarithms, the linear relationship

$$\ln \Delta R = \frac{P}{2}\ln\frac{1}{3} + \ln\frac{R^{\mathrm{S}}{}_{\mathrm{M-M}}}{3} \qquad (2)$$

is produced with

$$\Delta R = R_{\mathrm{M-M}} - \frac{2}{3}R^{\mathrm{S}}{}_{\mathrm{M-M}}$$

Assuming $R_{\mathrm{M-N}} = {}^1/_2R_{\mathrm{M-M}} + {}^1/_2R_{\mathrm{N-N}}$, a relationship for unsymmetrical linkages is achieved (3). With an

$$\ln \Delta R = -0.550P + \ln\frac{R^{\mathrm{S}}{}_{\mathrm{M-N}}}{3} \qquad (3)$$

appropriate distance (in 10^{-8} cm) for the single bond (or double or triple bond), a linear semilog plot of ΔR *vs.* P is obtained.

In our studies of dithiocarbamate and xanthate complexes of nickel(II) and their base adducts[4] we were impressed by the apparent relationships between the $(S_2)C$–N and $(S_2)C$–O distances and their infrared stretching frequencies. We were particularly interested in the mesomeric double-bond formation suggested by frequency shifts. Bernstein's relationship appeared appropriate to our considerations so we explored its validity for the CN and CO systems. Since the importance of NO as a ligand is now recognized,[5] we considered this bond also.

Equations of the form $\ln \Delta R = -0.550P + \ln (R^{\mathrm{S}}{}_{\mathrm{M-N}}/3)$ are obtained for CO, CN, and NO with $\ln (R^{\mathrm{S}}{}_{\mathrm{M-N}}/3)$ equal to −0.735, −0.700 and −0.789, respectively. Pauling[2b] covalent radii were used for the single-bond lengths needed to specify the equations. As Bernstein showed, "accepted" double- and triple-bond distances fit this relationship nearly exactly (Figure 1).

The usefulness of the Bernstein bond-order concept for first-row elements comes in applying it to observable physical properties (Table I). A property readily available for compounds containing CO, CN, and NO linkages is the infrared stretching frequency associated with these bonds. More appropriately, the force constant for the M–N bond should be a smoothly increasing function of increasing M–N bond order. However, force constants are not available from infrared data for most systems of interest. Yet, if the assumption is made that the square of the M–N stretching frequency, $\tilde{\nu}$, is a measure of the force constant, that is, if all dynamical effects are ignored, a smooth curve relationship between bond order and $\tilde{\nu}^2$ can be expected. As seen from Figure 2, smooth curves are achieved for a wide variety of compounds with known M–N distances and reported M–N stretching frequencies.

Some features of Figure 2 require special comment. If the assumption is made that the fractional bond order for $CO_3{}^{2-}$ and $RCO_2{}^-$ is obtained directly from the percentage double-bond character suggested considering only the equivalent valence bond structures for the ions, the points (CO; 6, 8) fall off the bond order *vs.* $\tilde{\nu}^2$ curve. Using experimentally obtained bond lengths for

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 112.

[2] (a) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965). Badger's rule (R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935)) has also been used.[2b] (b) L. Pauling "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948.

[3] H. J. Bernstein, *J. Chem. Phys.*, **15**, 184 (1947).

[4] D. Coucouvanis and J. P. Fackler, *Inorg. Chem.*, **6**, 2047 (1967).

[5] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

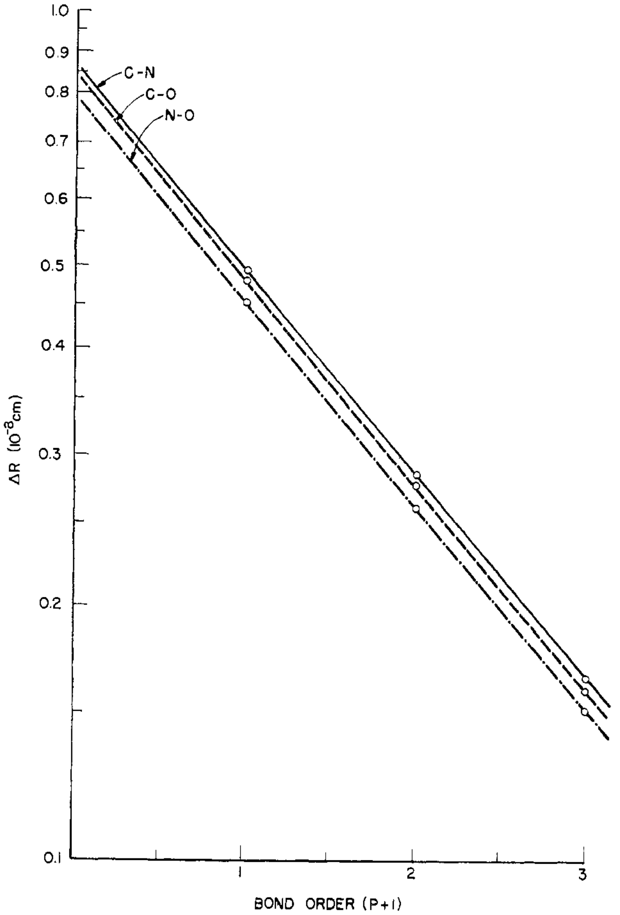

Figure 1.—Linear log plot of $\{R_{M-N} - {}^2/_3R^S{}_{M-N}\} = \Delta R$ *vs.* bond order for the M–N bonds CN, CO, and NO.

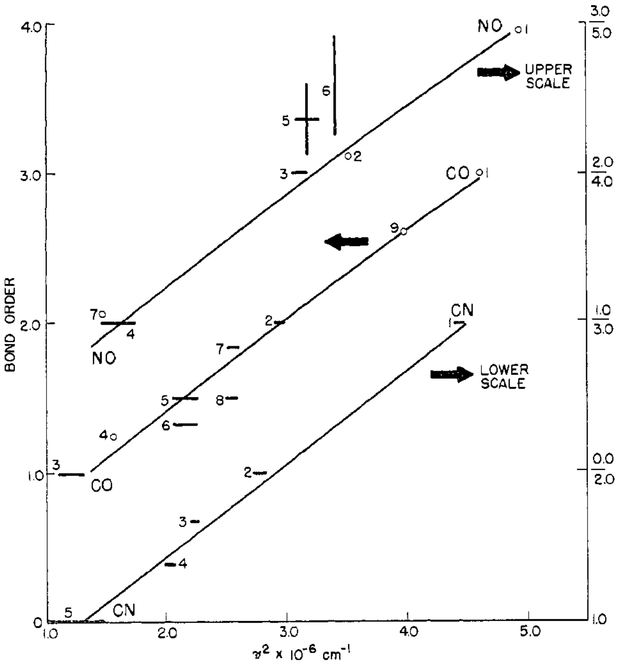

Figure 2.—Bond order *vs.* $\bar{\nu}_{M-N}{}^2$ for some compounds containing the M–N bonds CO, CN, and NO.

these ions, the Bernstein relationship gives bond orders which produce a good fit to the curve, bond orders which are ~15% higher than those suggested by the simple valence bond method.[6]

Table I

Data Used in Figure 2

No.	Bond	$\bar{\nu}$, cm^{-1}	Bond order	Ref
	Carbon–nitrogen			
1	Trible bond	2120–2160	3 (assumed)	*a*
2	Double bond	1640–1690	2 (assumed)	*a*
3	$Ni[S_2CN(C_2H_5)_2]$	1511	1.68 (1.325 ± 0.009 A)	*b, c*
4	$Ni(S_2CNH_2)_2$	1438	1.43 (1.38 ± 0.03 A)	*b, d*
5	Single bond	1000–1200	1 (assumed)	*a*
	Carbon–oxygen			
1	CO	2143	3 (assumed)	*a*
2	Double bond	1705–1725	2 (assumed)	*a*
3	Single bond	1050–1150	1 (assumed)	*a*
4	$Ni(S_2COC_2H_5)_2$	1250	1.22 (1.38 A)	*e, f*
5	$CaCO_3$	1429–1492	1.50 (1.31 A)	*g, h*
6	$CO_3{}^{2-}$	1429–1492	1.33 (assumed)	
7	$RCO_2{}^-$	1550–1610	1.84 (1.26 A)	*g, h*
8	$RCO_2{}^-$	1550–1610	1.50 (assumed)	
9	$Cr(CO)_6$	2000	2.00 (1.16 A)	*g, h*
	Nitrogen–oxygen			
1	NO^+	2220	2.96 (1.062 A)	*g, h*
2	NO	1876	2.12 (1.151 A)	*g, h*
3	$[Fe(NO)_2SC_2H_5]_2$	1743–1773	2.00 (1.17 A)	*i, j*
4	C_5H_5NO	1200–1300	1 (assumed)	*k*
5	$Fe(CO)_2(NO)_2$	1756–1810	2.36 (1.12 A)	*i, l*
6	$Co(NO)(CO)_3$	1825	~2.6 (1.1 A)	*i, l*
7	$[CuCl_2ONC_5H_5]_2$	1202	1.04 (1.346 ± 0.017 A)	*m, n*

[a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956. [b] See ref 4. [c] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19,** 619 (1965). [d] L. Cappachi, M. Nardelli, and H. Villa, *Chem. Commun.*, **14,** 441 (1966). [e] G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, **27,** 898 (1965). [f] M. Frazini, *Z. Krist.*, **118,** 393 (1963). [g] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963. [h] A. D. Mitchell and L. C. Cross, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958. [i] See ref 5. [j] J. T. Thomas, J. H. Robinson, and E. G. Cox, *Acta Cryst.*, **11,** 599 (1958). [k] S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19,** 189 (1963). [l] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, **33,** 1233 (1937). [m] W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4,** 97 (1965). [n] R. S. Sager, R. J. Williams, and W. H. Watson, *ibid.*, **6,** 951 (1967).

Available data for the two nitrosyls $Fe(CO)_2(NO)_2$ and $Co(NO)(CO)_3$ warrant reexamination. Since the bond lengths date from 1937 electron diffraction work, the data may be poor. This bond-order analysis suggests the complexes have longer NO bond lengths than the ones reported.

Finally, we emphasize again that no dynamical effects are considered in this treatment. Hence the position of single-bonded CO or CN on the frequency scale may be subject to considerable variation. In fact, some dynamical coupling must occur with the xanthates and dithiocarbamates also, although the effect appears to be minor in these compounds.

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(6) The Bernstein relationship appears to give a measure of the "true" bond order. In the calculation by Pauling[2b] of the bond length for $CO_3{}^{2-}$, resonance structures in addition to the three simplest ones are assumed along with suitable corrections for the charges on the atoms in some of these structures.

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Received August 24, 1967