σ and π Binding Effects in the Coordination of Carbon Monoxide and Comparison with Cyanide Ion

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Abstract: Semiempirical SCF calculations have been performed for a series of XCO and, for comparison, XCN molecules according to the structure of the CNDO/2 scheme. Computed CO bond orders and binding energies are found to correlate well with the CO stretching force constants. Examination of the results for HCO^+ and COH^+ reveals a role of the parent "lone-pair" orbitals for effecting an increase in CO bond order and binding energy upon adduct formation. Comparison of HCO^+ and COH^+ also reveals a fundamental difference in the role of the very stable 3σ MO of the parent in the two cases. For substituents with occupied π symmetry orbitals, charge transfer to CO *via* the π orbitals is found to be large, and the resultant CO bond weakening generally dominates σ stabilization. The computed "three-center" π MO's of XCO can be transformed to an equivalent basis of substituent π and parent π and π^* orbitals, and, in this basis set, back-donation to the parent by the substituent is easily accounted for as well as some π transfer in the direction parent-$\pi \rightarrow$ X. This analysis indicates considerable BH_3 and CH_3 hyperconjugation with CO in BH_3CO and CH_3CO^+. The results for BH_3CO, CH_3CO^+, HCO^+, and HCO^* indicate the operation of a synergic charge flow in the CO moiety. The operation of synergism in XCO is also seen by comparison of XCO with XCN. Both CO and CN are found to respond to adduct formation in similar fashion. Cyanide is computed to be the better donor and poorer acceptor although σ donation by CO is enhanced by back-bonding. Variation of the total bond orders and binding energies across both series of substituted molecules appears to be mainly due to changes in CN and CO π bonding. Further, while σ stabilization of CN^- is one consequence of carbon addition, an even more important source of increased CN stabilization appears to arise from a decrease in C–N repulsion as a result of charge withdrawal from the carbon atom. This mechanism is not so important for the isoelectronic but neutral CO.

In recent communications[1] we have reported the results of semiempirical LCAO–MO calculations for CN^- and a series of XCN molecules, where the substituent, X, is a single atom or methyl group. The choice of a series of simple-substituent cyano compounds was dictated by computing costs and ease of interpretation of the resulting charge distributions. Similar motivations are the basis of the selection of the XCO molecules to be discussed in this report. Most of the XCO molecules to be discussed have not previously been subjected to an LCAO–MO treatment.

The primary reasons for carrying through these calculations are to determine, according to the SCF formalism, the bases for commonly used concepts in discussions of the binding of substituents to carbon monoxide and to compare CO with the isoelectronic cyanide ion. The earlier calculations[1a–c] on the XCN compounds indicated that addition at either carbon or nitrogen results in increases (relative to CN^-) in the CN σ and total overlap energies. In molecules with extensive back-donation of π electron density to the cyano group, the total CN overlap energy decreases. The increases in σ covalent energies were linked to the unusual increases observed for the stretching force constants, relative to the parent CN^-, in those cases of weak or non-π donor substituents. Other aspects of the CN binding in the XCN series were tested by a comparison of experimental and computed electronic field gradients and nitrogen hyperfine coupling constants.[1d,e]

Contrary to these findings for cyano addition, discussions of the binding of carbon monoxide to a general substituent have focused on the π orbitals of the parent. Until recently,[2] it has been assumed that interpretative comparisons of XCO and CO vibrational frequencies do not require an accounting of differences in CO σ electron distribution. The question remains as to whether the differences in CO σ binding are negligible or simply subordinate to those of the CO π orbitals. These calculations were undertaken to bring more information to bear on this question and to compare the coordination properties of CO and CN^- within the basis of the LCAO–MO–SCF framework.

Computational Formalism

Calculations have been performed for the following molecules with their equilibrium geometries: CH_3CO^+,[3] CO,[4] BH_3CO,[5] HCO^* [6] (linear excited state), OCO,[7] H_2CO,[8] and NCO^-.[9] Calculations were also performed for HCO^+ and the hypothetical COH^+; since internuclear distances are not known for either of these species, the internuclear distances were varied and the results examined for variations with distance.[10] By comparison with CH_3CO^+ we have chosen to report

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[1] (a) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966); (b) K. F. Purcell, *ibid.*, **89**, 247 (1967); (c) *ibid.*, **89**, 6139 (1967); (d) *J. Chem. Phys.*, **47**, 1198 (1967); (e) *ibid.*, **48**, 5735 (1968).

[2] (a) G. R. Dobson, *Inorg. Chem.*, **4**, 1673 (1965); (b) D. J. Darensbourg and T. L. Brown, *ibid.*, 7, 949 (1968); (c) T. L. Brown and D. J. Darensbourg, *ibid.*, **6**, 961 (1967).

[3] F. P. Boer, *J. Am. Chem. Soc.*, **88**, 1572 (1966).

[4] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[5] W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

[6] G. Herzberg and D. A. Ramsey, *Proc. Roy. Soc.* (London), **A233**, 34 (1956).

[7] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[8] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[9] R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 1497 (1968).

[10] These results for both molecules are qualitatively, that is relative to differences between members of the XCO series, not changed over the range of CO distances 1.116–1.18 Å and CH or OH from 1.0 to 1.2 Å.

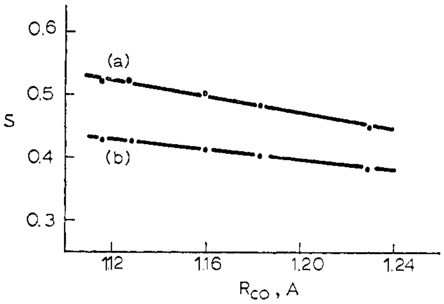

Figure 1. Overlap *vs.* CO distance: (a) 2 × (C_π, O_π), (b) (C_s, O_s).

only the results for HCO^+ in which H–C = 1.0 Å and C–O = 1.13 Å. To avoid, in a comparison of COH^+ and HCO^+, arbitrary differences in the wave functions due to differences in internuclear distances, we report only the results for C–O = 1.13 Å and O–H = 1.0 Å.

All calculations were subjected to the approximations of the self-consistent orbital population (SCP) technique discussed elsewhere[1e] and the SCF–CNDO formalism of Pople and Segal.[11] In spite of differences between the two formalisms, the conclusions are sufficiently alike to not warrant inclusion of both analyses. We report here on the CNDO results.

The molecular orbitals θ_i are written as linear combinations of atomic valence STO, ϕ_j

$$\theta_i = c_{ji}\phi_j$$

and Roothan's equations[12]

$$\mathbf{FC} = \mathbf{SCe}$$

are solved with variation of the c_{ji} to achieve a minimum in total energy of the molecule. The Fock matrix elements are given by, after incorporation of the CNDO/2 approximations

$$F_{jj} = U_{jj} + \left(P_{AA} - \frac{1}{2}P_{jj}\right)\gamma_{AA} + \sum_{B}(P_{BB} - Z_B)\gamma_{AB} \qquad (B \neq A)$$

$$F_{jk} = \beta_{AB}{}^{0}S_{jk} - \frac{1}{2}P_{jk}\gamma_{AB} \qquad (j \neq k)$$

where ϕ_j and ϕ_k are valence STO's on centers A and B, respectively. Definitions of terms and values for U_{jj} are given in the original papers.[11] The total energy of each molecule is given by

$$E_{\text{total}} = \sum_{A} E_A + \sum_{A,B} E_{AB} \qquad (B > A)$$

and we are primarily concerned with the term E_{AB} where A = carbon and B = nitrogen or oxygen. The atom pair energy may be dissected into covalent, ionic, and core contributions according to

$$E_{AB} = E_{AB}(\text{cov}) + E_{AB}(\text{ion}) + E_{AB}(\text{core}) = \sum_{jA}\sum_{kB}\left(2\beta_{AB}{}^{0}P_{jk}S_{jk} - \frac{1}{2}P_{jk}{}^{2}\gamma_{AB}\right) + (P_{AA}P_{BB} - P_{AA}Z_B - P_{BB}Z_A)\gamma_{AB} + Z_AZ_BR_{AB}{}^{-1}$$

In one section of our discussion we will have occasion to distinguish contributions to E_{AB}(cov) from σ and π atomic functions, and the summations over j,k in the last expression will then be factored accordingly.

In discussing the changes in CO and CN σ binding of these compounds, we will find it useful to examine the changes in 2s,2p hybridization at carbon and oxygen. These changes are measured in terms of the changes in atom polarizations, which, for each atom, are proportional to the atomic 2s,2p bond-order elements.[11] In all calculations the carbon atom is located at the origin with the other atom, oxygen or nitrogen, on the positive z axis. Consequently, the sign of P_{sp}, for either atom, is the same as the direction of atomic polarization along the molecular symmetry axis.

All calculations were performed on the "large core storage" IBM 360/50 system in our computing center. The program was obtained from QCPE and converted to double-precision arithmetic, and other desirable modifications were made.

Results and Discussion

Early evidence[13] for the relative unimportance of CO σ bond strength changes as a function of CO internuclear distance came from a comparison of C and O p orbital overlaps of σ and π symmetries as a function of CO distance. Over the complete range of experimentally observed CO distances, the σ overlap integral increases only very slightly with increasing CO distance, while the π integral very much more sensitively decreases.

There are two prime weaknesses in interpreting these results directly in terms of relative σ and π bond strength changes. Our calculations, as well as SCF computations[14] for CO, show that the C and O pσ orbitals contribute only about one-third of the CO binding electron density. The atomic pσ orbital character is concentrated mainly in the 4σ and 5σ MO's of CO, where their chief function is to remove electron density from the C–O binding region.[15] Consequently, the 3σ MO, which is comprised mainly of carbon and oxygen 2s atomic orbitals, is primarily responsible for the σ symmetry binding of carbon and oxygen. A very similar situation is found for cyanide.[1b,9] This being the case, an increase in CO internuclear distance would always lead to weakening of the CO bond because the 2s,2s overlap integral decreases as much as the 2pπ,2pπ overlap with increasing internuclear distance (Figure 1). Assuming[13] that the binding contribution of two overlapping orbitals is proportional to overlap integral, regardless of the particular pair of AO's, we would be forced to conclude that σ bond weakening is as important as π bond weakening as the CO distance increases; σ binding changes are not negligible. An additional weakness in using overlap integrals to infer relative σ and π changes is that no account is taken of the possibility that addition at the carbon atom also changes features other than overlap integrals of CO binding. Carbon atom addition can change the AO makeup of each MO and, for example, the carbon and oxygen pσ orbitals could make a greater contribution to CO binding in XCO than in the parent CO. A particularly significant possibility for unusual bonding effects arises for CO (and the isoelectronic

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[11] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[12] C. C. J. Roothan, *Rev. Mod. Phys.*, 23, 69 (1951).

[13] S. F. A. Kettle, *Spectrochim. Acta*, 1388 (1966).

[14] B. J. Ransil, *Rev. Mod. Phys.*, 32, 245 (1960).

[15] R. F. W. Bader and A. D. Bandrauk, *J. Chem. Phys.*, **49**, 1653 (1968).

CN^-, N_2, and NO^+) from the presence of a second nonbonding pair of electrons on oxygen.

Another objection may be raised regarding the vague and ill-defined relation between overlap integrals and binding energies. This question is especially meaningful when applied to the σ symmetry orbitals of CO where there are four possible pairs of carbon and oxygen AO interactions.

Bond Orders, Binding Energies, and Force Constants. Those XCO molecules for which F_{CO} is available are listed in Table I along with pertinent results from the LCAO-MO calculations. Graphical presentation of some of these results are given in Figure 2 from which it can be seen that there are smooth relations between CO force constants and both the computed bond orders and binding energies. These results are, therefore, in good agreement with chemists' use of force constants as an index of CO bond strength in carbonyl compounds. These plots have been used to make estimates of force constants for HCO^+, CH_3CO^+, HOC^+, and HCO^*, and these estimates are given in parentheses in Table I.

Table I. Binding Energies, Force Constants, Bond Orders, and σ–π Charge Densities for XCO

Compound	$-E_{CO}$, au	F_{CO}, mdyn Å^{-1}	P_{CO}	$P_{CO}{}^{\sigma}$	$P_{CO}{}^{\pi}$	Δq_{σ}	Δq_{π}[a]
HCO^+	2.05	(19.0)	3.84	1.95	1.89	−0.77	0.00
CO	2.00	18.6[b]	3.70	1.87	1.83	0.00	0.00
CH_3CO^+	1.94	(18.5)	3.69	1.95	1.73	−0.85	0.22
BH_3CO	1.92	18.0[c]	3.61	1.93	1.69	−0.61	0.24
COH^+	1.79	(16.5)	3.44	1.79	1.64	−0.56	0.00
HCO^*	1.74	(16.0)	3.35	1.94	1.41	−0.90	1.00
OCO	1.73	15.5[d]	3.31	1.94	1.36	−1.01	0.74
H_2CO	1.67	13.2[e]	3.16	1.91	1.25	−0.90	0.88
NCO^-	1.44	11.0[f]	2.85	1.92	0.93	−0.95	1.34

[a] Changes in total CO σ and π electron densities. [b] See ref 4. [c] S. Sundaram and F. F. Cleveland, *J. Chem. Phys.*, **32**, 166 (1960). [d] See ref 7. [e] L. Beckmann and L. Gutjahr, *Spectrochim. Acta*, **21**, 307 (1965). [f] See ref 9.

The basis for, and several interesting features of, these correlations become apparent through an examination of atomic orbital interactions where the interactions are separated on the basis of symmetry properties. Such a separation is not, however, unique, as has been fully expounded;[16] we use this method of factorization because of its established use by chemists.

It is apparent that somewhat competitive (in the sense of bond strengthening) forces are generally operative when addition occurs at the carbon atom. The CO σ bond order increases very slightly[2] (increase of 0.04 to 0.08) in all the XCO molecules treated here, in spite of considerable charge withdrawal by the substituents (seventh column of Table I). On the other hand, the CO π bond order decreases, relative to the parent CO, for all but HCO^+. Furthermore, the π bond order decrease (from 0.10 to 0.90) in some instances is considerably larger than the σ increase (but see the final section). Assuming that unit change in σ bond order implies a change in CO binding energy of about the same magnitude as the change due to unit change in π bond order (see below), we must conclude that changes in C–O π bonding tend to be larger than changes in σ bonding; *both* are important in cases of moderate X–CO π interaction while substituents capable of strong π interaction with CO (last column of Table I) tend to weaken the CO group more than strengthen it. This is a result of nearly constant σ CO bond order across the XCO series in Table I while the π bond orders change considerably across the series (see the top half of Figure 2). It is particularly interesting that, in spite of considerable variation in the amount of σ density donated by CO, there is very little variation in the σ CO bond order. These bond order implications are discussed further, and somewhat modified, in the last section of this discussion.

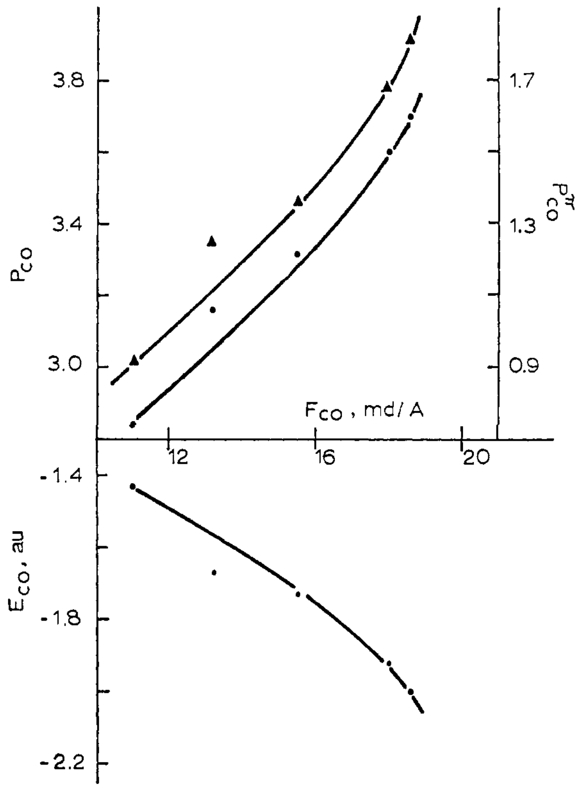

Figure 2. $E_{CO}, P_{CO}, P_{CO}{}^{\pi}$ *vs.* F_{CO}: ▲, $P_{CO}{}^{\pi}$, ●, P_{CO}.

HCO^+, to be more fully discussed later, is particularly interesting in that the substituent is incapable of π interaction with CO. The π bond order computed for this compound indicates some polarization of π density toward the carbon, as expected. Consequently, σ-only coordination of CO leads to a stronger CO bond by both σ and π mechanisms.[2a] Similarly, COH^+ shows even more pronounced polarization of CO π density toward the oxygen atom. Both polarizations may be alternately interpreted in terms of the valence-bond π resonance forms with I making an enhanced contribution in the case of COH^+ and II making an enhanced contribution in HCO^+. Interestingly, the CO

$$\underset{\text{I}}{:C{=}\ddot{O}:} \longleftrightarrow \underset{\text{II}}{:C{\equiv}O:}$$

σ bond order of COH^+ is also appreciably reduced and leads us to suspect that, should efforts to prepare Lewis acid adducts of metal carbonyl complexes, in which the acid coordinates to the oxygen of carbon coordinated

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(16) C. Trindle and O. Sinanoglu, *J. Chem. Phys.*, **49**, 65 (1968), and references therein.

Table II. σ Orbital Results for CO, HCO^+, and COH^+

MO	q_C[a]	$P_{sp}{}^{C}$[b]	q_O[a]	$P_{sp}{}^{O}$[b]	P_{CO}	q_H	P_{AH}
			Carbon–Oxygen σ Bond				
CO 3σ	0.60	0.30	1.40	−0.28	1.51		
HCO^+ 3σ	0.62	0.30	1.36	−0.26	1.52	0.01	0.02
COH^+ 3σ	0.50	0.24	1.39	−0.20	1.18	0.11	0.33
			Oxygen Lone Pair				
CO 4σ	0.61	−0.04	1.39	0.60	0.32		
HCO^+ 5σ	0.46	−0.02	1.32	0.46	0.41	0.22	0.34
COH^+ 4σ	0.40	0.06	1.22	0.32	0.55	0.38	0.85
			Carbon Lone Pair				
CO 5σ	1.57	−0.78	0.44	0.06	0.04		
HCO^+ 4σ	1.02	−0.44	0.45	0.22	0.02	0.53	1.01
COH^+ 5σ	1.75	−0.86	0.19	−0.06	−0.09	0.07	0.07
CO ($4\sigma + 5\sigma$)	2.19	−0.82	1.82	0.66	0.36		
HCO^+	1.48	−0.42	1.77	0.68	0.43	0.75	1.35
COH^+	2.15	−0.92	1.41	0.26	0.46	0.45	0.92

[a] q_A = number of electrons in s,p AO's of atom A. [b] $P_{sp}{}^{A}$ = s,p bond-order matrix element of atom A.

CO, be successful,[17] the infrared spectra of the adduct will be characterized by a pronounced lowering, relative to the carbonyl complex, of the CO stretching frequency. Furthermore, enhanced back-bonding from the metal to CO would compliment polarization of the CO π density, particularly in view of the anticipated increase in CO distance. The decrease of CO frequency should, in any event, amount to at least a few hundred wave numbers.

H_2CO is an interesting variant in the series, in that the hydrogen atoms form the basis for one σ and one π symmetry orbital for interaction with CO. Inclusion of this molecule in the correlations of Figure 2 does not change the qualitative nature of the correlations but, quantitatively, gives each curve a sigmoid appearance. The molecule fits well into the series and, again, it is the change in π binding which is most important. Interestingly, the response of the CO σ system to the presence of two hydrogen nuclei is very little different from the other cases. The variant character of formaldehyde as a member of the series of XCO molecules is most evident when viewed from an individual MO basis. The π orbital perpendicular to the molecular plane reveals the effects of σ charge withdrawal in that this orbital, like those of HCO^+, is polarized toward the carbon atom with an increased bond order of 0.99. The in-plane π orbitals show the effects of "back-donation" in that the CO bond order due to in-plane carbon and oxygen $p\pi$ orbitals is greatly reduced to 0.27. The latter is a net bond order due to two occupied MO's; the lower energy of these is CO binding (decreased bond order of 0.73) while the higher energy MO is CO antibinding (bond order = −0.47) and $(H)_2$–C binding (bond order = 0.45). This orbital is usually thought of as being "localized" on the oxygen atom and is usually called an oxygen "lone pair." The small net in-plane CO π bond order is, thus, a result of both the reduced bond order from the CO binding MO and the negative bond order from an orbital exhibiting the characteristics of the parent π antibonding MO. Later we will see that the two in-plane π MO's of H_2CO bear a strong resemblance to the (four) π MO's of the other members of this series. That H_2CO should alter the correlations of Figure 2 is not particularly surprising when one considers that the CO binding changes are dominated, on the one hand, by an out-of-plane π orbital polarized toward carbon with increased bond order and, on the other, by an in-plane π MO of reduced CO bond order and a second in-plane π MO with a negative CO bond order.

Changes in σ Binding. While the changes in σ bond orders are computed to be small, it is interesting to examine the reasons for this and for the increase in bond order from a detailed point of view. The simplest members of the series for this purpose are those in which the substituent is hydrogen: HCO^+, HCO^*, and COH^+. The latter is included in this discussion because it appears (Table I) to be uniquely different from the two carbon-substituted species, which have very similar σ orbitals. The pertinent data are given on a MO basis in Table II.

The 3σ MO of the parent CO is computed to lie at a very low energy and consists mainly of the oxygen 2s orbital. The atom polarizations indicate some hybridization of carbon and oxygen to facilitate carbon–oxygen bonding. As indicated by the bond order, the greatest part of the CO σ binding arises from this MO. The 4σ MO is predominantly oxygen 2s,2p in character; in spite of the oxygen hybridization in a direction away from the binding region (suggesting the "oxygen lone pair" nature of the orbital), a significant CO bond-order contribution does arise in this MO. The 5σ MO is heavily carbon atom in character, and there is considerable mixing of the carbon 2s,2p atomic functions (the carbon "lone pair") to direct electron density away from the CO binding region. This orbital is essentially nonbonding. The high carbon atom polarization in the 5σ MO is responsible for a computed net lone-pair moment[11] for CO in a direction away from the oxygen atom. In fact, the molecular dipole moment computed for CO (1.0 D) points in the direction $\overleftarrow{\mathrm{CO}}$ (this computation considers only the total atom charges and the atom polarizations).

Upon protonation at the carbon atom all the MO's move to much lower energy in keeping with the "Madelung term" effect of the unbalanced hydrogen nuclear charge. The 3σ MO is virtually unperturbed by the presence of the proton as evidenced by the atom charges, hybridization moments, and bond orders. Consequently, the 3σ MO may be considered a "core"

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[17] (17) Work being pursued toward this end in another group of this department (J. C. Kotz) has yielded promising preliminary results.

MO for this molecule. This is a major reason for the smallness of the change in CO σ bond order for each of the molecules in the series. Considerable polarization and rehybridization occurs, however, in the 4σ and 5σ MO's. This complicates an interpretation, based on the parent MO's,[18] of the effects of carbon atom substitution. However, from comparison of oxygen atom charges, hybridization moments, and CO bond orders from the 4σ and 5σ MO's of HCO^+ and CO, it appears that the 5σ MO of HCO^+ is most like the 4σ MO of the parent, while 4σ of HCO^+ bears a strong resemblance to 5σ of CO. Such a correlation of MO's, while not rigorous, fits our ideas regarding coordinate bond formation by the higher energy "carbon lone pair" of electrons. Considered together ($4\sigma + 5\sigma$), almost all of the charge donated to H^+ by CO is seen to come from the carbon atom, while the oxygen σ density is reduced by *ca.* 0.1 electron. In addition, the net atomic polarization of the carbon is more balanced and much reduced relative to the parent as a natural consequence of the electron-attracting power of the hydrogen nucleus. There is no longer a need for carbon hybridization as a means of removing "nonbinding" electron density from the CO internuclear region. This net reduction in hybrid moment at carbon arises in the 4σ MO of HCO^+ which we have approximately identified as the original carbon "lone pair," 5σ, of CO. It appears that almost all of the σ bond order increase arises from what can be referred to qualitatively as the "oxygen lone pair" orbital of the parent. In terms of carbon and oxygen atomic orbital interactions, the principle source of this increase is enhanced C 2s–O 2p interaction (Table III). *In short, it seems that polarization of the "oxygen lone pair" orbital toward carbon is the prime reason for the increase in CO σ bond order upon carbon substitution.*

Table III. Changes[a] in Total AO Pair Bond Orders

	O_S	O_σ
C_S		
HCO^+	+0.05	+0.16
COH^+	−0.01	−0.03
C_σ		
HCO^+	−0.05	−0.08
COH^+	+0.10	−0.12

[a] Relative to the parent bond orders of: C_S–O_S, 0.30; C_S–O_σ 0.38; C_σ–O_S, 0.52; C_σ–O_σ, 0.66.

Turning now to COH^+, we find considerably different responses in the σ MO's of the parent to oxygen substitution. The most striking difference between HCO^+ and COH^+ is the role of the 3σ orbital. Roughly 25% of the total OH bond order and 20% of the H charge density arises from this orbital. The carbon and oxygen hybridization moments change very little on addition at oxygen, and the oxygen charge density in this MO is essentially unaffected. The charge transfer of 0.1 electron to the proton in the 3σ MO comes from the carbon atom! Even more important is the decrease in CO bond order due to this orbital. The 3σ MO is no longer "inert," and this involvement with the proton is most reasonably linked to better "overlap" of the H 1s orbital with the 3σ MO when the proton is in the vicinity of the oxygen than when in the vicinity of the carbon. The 4σ and 5σ orbitals together exhibit very little change in carbon density and hybridization. The 0.45 electron transferred to the proton comes almost entirely from the oxygen atom and results in an OH bond order of 0.92. As noted above for the carbon atom in HCO^+, the oxygen hybridization moment appreciably decreases. Similarly, the ($4\sigma + 5\sigma$) CO bond order increases (+0.10) but insufficiently to offset the decrease (−0.33) in 3σ bond order. By arguments similar to those used for HCO^+, we may approximately correlate 4σ and 5σ of CO with 4σ and 5σ, respectively, of COH^+. The main OH bond forming orbital (4σ) exhibits considerable charge transfer from both carbon and oxygen with a change in hybrid moment direction at carbon, a sharp decrease in oxygen moment (as expected), and a sizable *increase* (+0.23) in CO bond order. In terms of total atomic orbital interactions (Table III), the increase stems primarily from enhanced O_{2s}–C_{2p} bonding. To accommodate this charge flow toward OH in 3σ and 4σ, the 5σ orbital is polarized primarily toward carbon and gives a small negative CO bond order.

In summary, the "lone-pair" 4σ and 5σ MO's, taken together, respond similarly to protonation at either carbon or oxygen with an increase in CO bond order. COH^+ differs from HCO^+ mainly in the different response of 3σ which is virtually unperturbed for carbon addition and polarized, in the case of oxygen addition, to decrease the CO bond order. This behavior on carbon substitution is similar to that reported for the isoelectronic[1b] cyanide ion. The role of the "lone-pair" orbitals is important to an understanding of the unique, enhanced σ binding of CO and CN^- upon addition at either atom. A point of consistency is that the origin of increased ($4\sigma + 5\sigma$) bond order for both HCO^+ and COH^+ is the enhanced binding between the donor atom 2s orbital and the "other atom" 2p orbital, in agreement with Bent's isolvalent hybridization arguments.[19]

Changes in π Binding. (a) BH_3CO and CH_3CO^+. The C_{3v} symmetry molecules were included in these calculations not only because they are examples of carbon atom coordination of carbon monoxide but also because of the question of hyperconjugation of BH_3 and CH_3 groups with CO.

$$H_3{\equiv}M{-}CO \longleftrightarrow H_3{=}M{=}CO$$

The borine group of borine carbonyl has HBH angles sufficiently greater than tetrahedral[5] to have caused speculation about significant interaction of the BH bond density with the π orbitals of CO. Similarly, an unusually short C–C bond distance has been reported[3] for the methyloxocarbonium ion. This raises the question of the extent of e symmetry orbital interaction between methyl and CO.

The results of the calculations to be used in this discussion are set out in Table IV. To obtain an accurate indication of the borine and methyl interactions with CO, calculations were performed for these groups *with the angles and distances found in the CO adducts.* In this way we eliminate from consideration

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[18] An alternative analysis, based on mixing of parent CO 3σ, 4σ, 5σ, and 6σ molecular orbitals, of σ bonding changes could be given (see the later discussion of XCO π bonding). We retain the approach used here because of chemists' general use of a σ polarization concept.

[19] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Table IV. Charge Distributions and Bond Orders in BH_3CO and CH_3CO^+ by Symmetry Orbitals

		MH_3 a_1	MH_3 e
BH_3	H	1.00	2.21
	B	1.00	1.79
BH_3CO	H	1.04	2.01
	B	1.57	1.75
$P_{(H_3)C}$			0.80
$P_{B,C}$		0.79	0.65
CH_3^+	H	0.83	1.66
	C	1.17	2.34
CH_3CO^+	H	0.90	1.60
	C	1.95	2.18
$P_{(H_3)C}$			0.64
$P_{C,C}$		0.88	0.67

any electron density rearrangement in the MH_3 moiety which results from a change in structure of that group.

The bond orders given in Table I show that the CO π bond orders of both compounds decrease and, in view of the opposite π bond order change of HCO^+, this implies "back-bonding" or hyperconjugation in the MH_3CO compounds. However, this is not necessarily a valid conclusion (see next section) and direct evidence for hyperconjugation comes from the computed (carbon + oxygen) π orbital electron density increases (column 8 of Table I) of 0.2 electron for both compounds. That the CO π occupation numbers should be nearly the same for both of these compounds is initially surprising. The density distributions in the nonplanar borine and methyl groups are quite different, however, and, along with the difference in σ donation by CO in the two compounds, can serve as a basis for explaining this result.

Both borine and methyl cation have unoccupied orbitals of a_1 symmetry which are essentially pure 2p orbitals. The net σ charge transfers of 0.61 and 0.85 electron from CO to BH_3 and CH_3, respectively, are to the boron and carbon atoms with only small increases in hydrogen atom densities. The unusual bonding effects occur in the π or e symmetry orbitals. In borine the electron density of these orbitals is more concentrated at the hydrogens than at boron, while in the methyl cation this electron density is distributed more heavily on carbon than on the hydrogens. Interaction of borine with CO results in a net charge transfer of about 0.2 electron from the hydrogens to CO with an H_3–C bond order of 0.80. That the electron density transferred to CO by borine comes almost entirely from the hydrogens and that the B–C π bond order is 0.65 are in keeping with the hyperconjugative resonance form. The B–C π bond order indicates (very roughly) a 30% contribution of this π resonance structure. In the case of methyl cation interacting with CO, there is a net transfer of 0.23 electron to CO *via* the π orbitals of methyl, but the carbon, rather than hydrogen, AO's serve as the primary source of this density. Less methyl hydrogen atom involvement in the "back-bonding" than is the case of borine carbonyl is also indicated by the smaller H_3–C bond order of 0.64. That this difference in the role of hydrogen atoms is not simply one of distance from the carbonyl carbon is evident from the H–C distance of 2.17 Å in borine carbonyl and 1.95 Å in methyloxocarbonium. The difference appears to be more directly related to the stronger, shorter "adduct" bond in the cation, the greater σ charge transfer by CO to methyl, and the difference in electron distribution in the distorted, free borine and methyl cation species. It is interesting to note that while the C–C σ bond order is greater than the B–C σ bond order, the π bond orders (0.67 and 0.65, respectively) are closely the same. It appears that CO makes a greater demand for π density from methyl than from borine as a result of the greater σ transfer to methyl, in keeping with electroneutrality and orbital electronegativity principles. The demand can be met because the e symmetry orbital density is originally more concentrated on the carbon of methyl. The net result is similar back-donation of electron density by CH_3^+ and BH_3. Thus, synergic charge flow appears to be of considerable importance in a comparison of the binding of borine and methyl cation to CO. Finally, we note that the ratios of e:a_1 charge transfers are not the same for BH_3 and CH_3^+ (0.39 and 0.26, respectively) and are in line with the expected relative electron-attracting abilities of BH_3 and CH_3^+.

(b) The XCO Series. As indicated, in Table I, by the changes in CO π atomic orbital densities for each molecule having a substituent with occupied π orbitals, there is considerable "back-donation" to the carbonyl group. Traditionally, this "excess" electron density on CO (last column of Table I) would be attributed to occupation of the parent π^* MO's. Such a view point appears to be consistent also with the computed CO π bond order decrease with increasing excess electron density. For HCO*, π^* occupation is certainly the case, with the odd electron occupying a π orbital computed to be very much like the antibonding orbitals of the parent. In comparing this molecule to the analogous HCO^+ cation, we note two interesting features. (1) The cation C–O distance is 1.13 Å while that of the radical is considerably longer, 1.18 Å; in spite of this, the total CO σ bond orders of the two compounds are very close. (The same phenomenon persists in NCO^- where the C–O distance is 1.23 Å.) (2) The extra electron in π^* assists charge donation by CO to the proton; such a comparison of HCO^+ and HCO* illustrates a synergic relation between total π and total σ density in CO.

Each of the other substituents in this series may be viewed as back-donating electron density to the CO parent. To facilitate an analysis of the π binding in the molecular series from just this point of view, each of the occupied molecular π orbitals, originally in an AO basis, may be cast in the form of linear combinations of substituent atomic orbitals with parent π_{CO} and π_{CO}^* molecular orbitals. The results of such a transformation for each molecule are given in Table V where it is seen that *both* π_{CO} and π_{CO}^* are mixed into each XCO π molecular orbital. The π_b and π_n notation to distinguish occupied XCO molecular orbitals is based on a three-center description of the π bonding. Inspection of the MO's in an atomic orbital basis readily reveals that the highest occupied pair of degenerate π orbitals in each case closely resembles a nonbonding three-center molecular orbital. These π_n orbitals possess a node near the carbon atom and, accordingly, opposite parity at the terminal (X, O) atoms, as must be rigorously true for OCO. Furthermore, the signs of the X and parent π_{CO}^* coefficients in these MO's are the same and opposite that of π_{CO}. Likewise, in

Table V. π Molecular Orbital Eigenvectors of XCO in the Parent π_{CO} and π_{CO}^* Basis[a]

	MO	H_1–H_2	X	π_{CO}	π_{CO}^*	π_{CO}^{occ}	π_{CO}^{*occ}	$P_{X\pi}$	$P_{X\pi^*}$
CH_3CO^+	π_b	0.258	0.489	0.774	0.166	3.98	0.24	0.12	0.89
	π_n	0.365	0.553	−0.629	0.181				
BH_3CO	π_b	0.172	0.298	0.919	0.085	3.99	0.25	0.18	0.66
	π_n	0.471	0.591	−0.389	0.236				
HCO*[b]	π_1^α			1.000	0.011	4.00	1.00		
	π_2^α, π_1^β, π_2^β			0.999	0.033				
	π_3^α			−0.033	0.999				
OCO	π_b		0.562	0.802	0.205	3.98	0.76	0.12	1.55
	π_n		0.707	−0.594	0.384				
H_2CO	π_1 (out-of-plane)			0.992	0.129	3.85	1.03	0.45	1.33
	π_b	0.365		0.833	0.201				
	π_n	0.383		−0.499	0.676				
NCO^-	π_b		0.512	0.832	0.211	0.391	1.43	0.35	1.85
	π_n		0.635	−0.533	0.560				

[a] The last four columns are total ($\pi_b + \pi_n$) quantities. [b] The superscripts α and β designate the spin functions of the various spin orbitals.

Table VI. Binding Energies, Force Constants, Bond Orders, and σ,π Charge Densities for XCN

Compound	$-E_{CN}$, au	F_{CN},[b] mdyn Å^{-1}	P_{CN}	P_{CN}^σ	P_{CN}^π	Δq_σ[a]	Δq_π[a]
HCN	2.24	18.7	3.97	1.97	2.00	−0.93	0.00
CH_3CN	2.19	18.1	3.91	1.97	1.94	−0.98	0.05
CH_3NC	2.08	16.7	3.75	1.89	1.86	−0.87	0.00
CN^-	2.08	16.4	3.92	1.95	1.98	0.00	0.00
OCN^-	2.05	15.5	3.72	1.96	1.76	−0.98	1.37
NCN^{2-}	1.75	11.8	3.35	1.94	1.40	−0.91	0.88

[a] Changes in total CN σ and π electron densities. [b] See ref 1b,c for original citations.

compliance with another general feature of the three-center description, the phases of π_{CO} and π_{CO}^* in π_b are the same at carbon; this results in a "pile up" of electron density on the central atom in this MO. An examination of the π_b and π_n orbitals shows them to bear very little resemblance to either the π_{CO} or the π_{CO}^* orbitals; with a node at the carbon atom in the π_n orbitals, it would appear that nearly all XC binding occurs *via* the π_b orbitals, and the CO π bond order for these orbitals is greatly reduced from that of π_{CO}. The alternate method of describing the π binding in these molecules in terms of π_{CO} and π_{CO}^* orbitals is, of course, equivalent and perhaps easier to accomodate in terms of qualitative ideas concerning back-bonding in CO adducts. Such an approach does emphasize, moreover, the pronounced mixing of π_{CO} and π_{CO}^* into both π_b and π_n of XCO, and therefore the "noncore" character of the π_{CO} orbitals.

The seventh and eighth columns of Table V list the parent π_{CO} and π_{CO}^* occupation numbers on the basis of the alternate description. The π_{CO} occupation numbers are quite close to 4.0 in most cases and indicate little net charge transfer[2a] to X from π_{CO}. Therefore, the π_{CO}^* occupation numbers are quite close to the "excess" π densities of Table I. Exceptions occur in the cases of NCO^- and H_2CO where the XC distance is short and the CO distance long. In these two instances, particularly H_2CO, there is considerable charge transfer from π_{CO} and even greater back-donation from X to π_{CO}^* than indicated by the "excess" π densities. To complete the π system description, the last two columns of Table V list the X,π_{CO} and X,π_{CO}^* bond orders. The small values computed for X,π_{CO} are the net result of large but nearly cancelling bond orders in π_b and π_n. These values indicate, as do the parent π_{CO}^* occupation numbers of Table V, the extent of back-bonding in this series and further augment the discussion of hyperconjugation in borine carbonyl and methyloxocarbonium.

Comparison of Isoelectronic XCN and XCO Molecules. The next aspect of our calculations which we would like to discuss is a comparison of several of the XCO compounds with the corresponding XCN analogs. Before making the comparison we need to present and discuss the results of the CNDO computations for HCN, CH_3CN, CH_3NC, CN^-, OCN^-, and NCN^{2-}. As was done for XCO, the results bearing on a correlation between CN force constant and CN bond orders and binding energies are given in Table VI and Figure 3. A linear correlation between binding energy and force constant is seen to be followed over a considerable range of force constants. The same is true of a relation between force constant and total bond order for all but CN^- which has a computed bond order greater than all series members except HCN. A similar situation was encountered in earlier SCP calculations.[1b] Analysis of the SCP calculations was based on Mulliken's overlap populations and overlap energies and, while the overlap energies correlated well with force constants, the overlap population computed for CN^- was larger than that computed for all series members except HCN. This discrepancy between bond order and energy would appear to result from the characteristic of a bond order to index the covalent binding energy and not include the repulsive "ionic" contribution to the cyanide diatom binding energy. This problem will be discussed more fully later; at this point we note that both the carbon and nitrogen atoms of cyanide carry excess negative charge and the repulsion would not be indexed by the bond order but would be included in the binding energy. This is not a problem with NCN^{2-} and OCN^- since the carbon atoms in these molecules bear a small charge[9] (see next section).

Many of the features of Table VI are similar to those of Table I for XCO; the CN σ bond order tends to increase only slightly, in spite of considerable electron withdrawal by the substituent, when the latter is bonded

Table VII. π Molecular Orbital Eigenvectors of XCN in the Parent π,π^* Basis[a]

	MO	H_1–H_2	X	π_{CN}	π_{CN}^*	π_{CN}^{occ}	π_{CN}^{*occ}	$P_{X,\pi}$	P_{X,π^*}
CH_3CN	π_b	0.380	0.608	0.568	0.139	3.96	0.09	0.23	0.41
	π_n	0.320	0.353	−0.818	0.048				
CH_3NC	π_b	0.373	0.604	0.589	−0.119	3.93	0.06	0.26	0.26
	π_n	0.340	0.365	−0.798	0.018				
OCN^-	π_b		0.583	0.800	0.145	3.99	0.39	0.06	1.17
	π_n		0.752	−0.598	0.277				
NCN^{2-}	π_b		0.529	0.834	0.103	3.93	0.89	0.24	1.52
	π_n		0.707	−0.537	0.461				

[a] The last four columns are total ($\pi_b + \nu_n$) quantities.

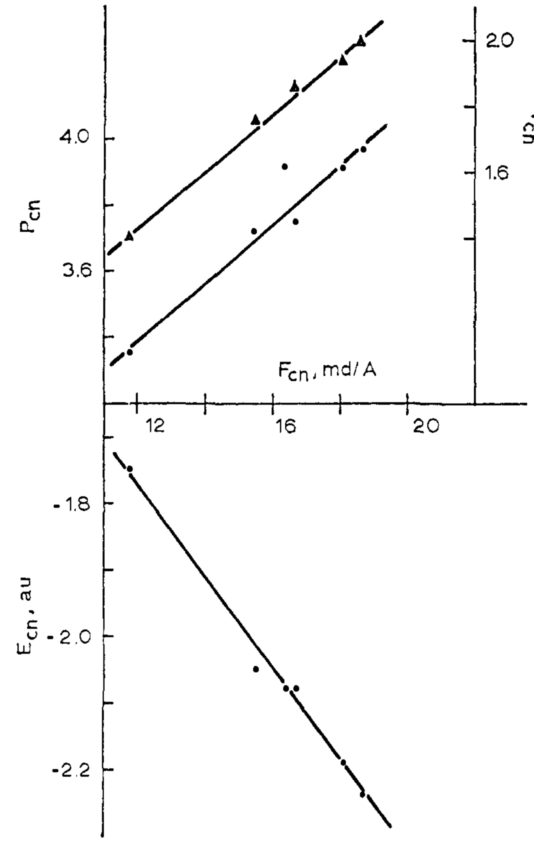

Figure 3. $E_{CN}, P_{CN}, P_{CN}^{\pi}$ *vs.* F_{CN}: ▲, P_{CN}^{π}; ●, P_{CN}

to carbon. The π bond order is very much reduced when the substituent is either of the "back-bonding" atoms, oxygen or nitrogen. Both the σ and π bond orders decrease in methylisonitrile, the "linkage isomer" of acetonitrile, and yet the CN force constant and binding energy change very little. Judging from the excess CN π density (last column of Table VI) in this compound, there seems to be no hyperconjugation of the methyl group with CN when the former adds to the nitrogen atom. The results of analyses of the π molecular orbitals on the basis of parent π_{CN} and π_{CN}^* orbitals are given in Table VII. The occurrence of back-bonding is now evident for all of these compounds, and it is seen that the net zero charge transfer in the π orbitals of methylisonitrile is the result of equal donation and acceptance to and from methyl by π_{CN} and π_{CN}^*, respectively. That the methyl carbon, π_{CN}^* bond order is smaller for the isonitrile than for the nitrile is readily understood as a consequence of poorer overlap of the methyl carbon orbitals with π_{CN}^* in the former instance.

In comparing the responses of CN^- and CO to a common substituent at the carbon position, almost all of the differences, according to the CNDO scheme, are questions of magnitude of effect. The differences in magnitudes can be very simply related to the difference in the effective nuclear charges of nitrogen and oxygen. Some of the computed quantities which are useful in making a comparison are collected in Table VIII, for convenience. Where back-bonding is of moderate or no importance (X = H, CH_3), the σ donation by cyanide is greater than that of carbon monoxide (second and third columns of Table VIII); the operation of synergism in CO is apparent for X = O, N as indicated by the relative increase in CO σ donation when back-donation to π_{CO}^* is great. The data in Table VIII for the XCN molecules reveal no tendency toward synergic charge flow in CN.[1c] The greater σ donation by CN^- is due to less nuclear charge in this species and is manifest in a lower electronegativity and also a greater carbon charge density for CN^- than CO. Also directly related to the greater nuclear charge of oxygen than nitrogen is the higher amplitude of the π_{CO}^* orbital at carbon than that of the π_{CN}^*, a feature which favors and partially accounts for greater back-bonding to CO.

Table VIII. Comparison of CN and CO Bonding Changes on Substitution at C[a]

Substituent	Δq_σ^{CN}	Δq_σ^{CO}	Δq_π^{CN}	Δq_π^{CO}	ΔE_{CN}, au	ΔE_{CO}, au
H	−0.93	−0.75			−0.16	−0.05
CH_3	−0.98	−0.85	0.05	0.23	−0.11	0.05
O	−0.98	−1.00	0.37	0.74	0.03	0.26
N	−0.92	−0.94	0.88	1.37	0.33	0.56

[a] Entries in this table are differences between the substituted molecule and the corresponding parent.

Also apparent from the last two columns of Table VIII is the greater stabilization of CN than CO by non or weakly π bonding substitutents and the greater destabilization of CO from good π bonding substituents.

Table IX shows that CO bonds the same carbon substituent more tightly than does CN^- when that substituent possesses π symmetry orbitals. This does not mean, however, that C–X σ binding is unimportant

Table IX. X–C Bonding in XCN and XCO

	P_{XC}^{σ}		P_{XC}^{π}		$-E_{XC}$, au	
X	CN	CO	CN	CO	CN	CO
H	1.40	1.36			0.78	0.69
CH_3	1.94	1.90	0.46	0.67	1.19	1.30
O	1.92	1.94	1.92	1.36	1.43	1.73
N	1.94	1.96	1.40	1.76	1.75	2.05

for either compound or that C–X π interaction dominates the C–X interaction but that π binding between substituent and carbon is of considerably greater importance for CO than CN^-.

The similarities in X and π_{AB} eigenvectors for OCO, OCN^- and NCO^-, NCN^{2-} in Tables V and VII are striking. The $\pi_{CN}{}^*$ coefficients are consistently smaller than $\pi_{CO}{}^*$ in both π_b and π_n, pointing up the difference in π-acceptor properties of CN and CO. Similarly, hyperconjugation is seen to be of considerably greater importance in CH_3CO^+ than in CH_3CN.

Bond Ordering and Binding Energy. In the preceding discussions we have relied heavily on computed CO and CN bond orders to index the effects of carbon and oxygen (nitrogen) substitution. At several points we cautioned that the use of bond orders could be ambiguous and perhaps misleading. In a very strict sense we should examine the change in CO and CN binding energies, both σ and π, but the quantity E_{AB} is complex with contributions from several sources while bond orders seem to hold more meaning for most chemists. Therefore, as long as the colvalent binding energy contribution to E_{AB}, or more correctly *changes* in covalent binding energy, dominate along the XCO and XCN series, we are somewhat justified in focusing our attention on bond-order parameters to follow the changes in CO and CN binding. In demonstrating a relation between binding energy and force constant for each of these molecules, we are necessarily dealing with an empirical relation, since a force constant is rigorously defined in terms of the potential surface curvature at the energy minimum. On the other hand, the ground-state electron distribution is reflected, on an energy scale, by E_{AB}, and the force constant, F_{AB}, is a ground-(electronic) state property of the molecule. Bader and Bandrauk[15] have, in fact, presented evidence to show that the magnitude of a force constant is intimately related to the ground-state molecular charge distribution and that the static forces acting on the nuclei in molecules are closely related to the changes in these forces with nuclear displacement. We should, therefore, not be surprised to find a close relation between F_{AB} and E_{AB} which is conceptually more easily handled than a relation between either of these and the corresponding bond dissociation energy (as experimentally or theoretically defined).

As shown in the Computational Formalism section, the quantity E_{AB} is a composite of "attractive" and "repulsive" energies consisting of the covalent term, the core repulsion term, and the "ionic" term which, in turn, is comprised of electron repulsion and electron–nuclear attraction terms. As a direct consequence of the CNDO/2 approximations, unit bond order between any two AO's on two atoms will tend to give rise to the same contribution to the covalent term because $\beta_{AB}{}^0$ and γ_{AB} are "average" quantities and the same for both σ and π AO's on the two centers. Nevertheless, the bond order and covalent binding cannot be quantitatively proportional because, in the CNDO framework, of the second-order dependence of covalent energy on bond order and also because of the appearance of the overlap integral in the expression for the covalent binding energy. In this way, the CNDO/2 formalism allows for a difference in the contribution from, say, 2s–2p interaction on the one hand and 2pπ–2pπ on the other. No distinction is made between s, pσ, and pπ in the "ionic" term. As a result, the E_{AB} (and the P_{AB} for that matter) presented here only approximates the values one would obtain from "approximation free" SCF calculations using the same minimal STO basis sets. This constitutes a criticism of the use of CNDO E_{AB} to index binding energy changes between C, O and C, N, since the relative contributions of σ and π orbitals to the binding and total energies are not exactly what they should be. Bearing this in mind, and also that we are dealing with structurally closely related molecules in the XCO and XCN series, we have adopted a more or less empirical approach to the results of these computations.

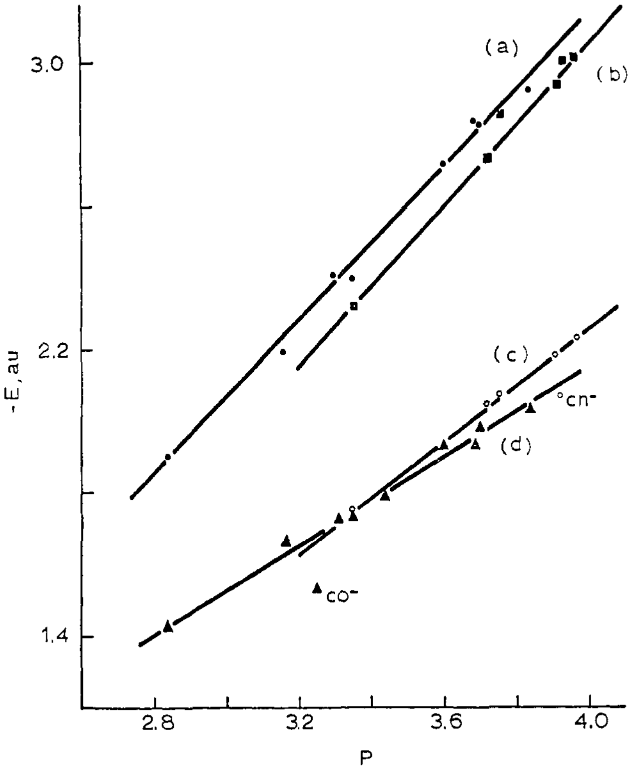

Figure 4. Diatom energy *vs.* bond order: (a) $-E_{CO}$(cov); (b) $-E_{CN}$(cov); (c) $-E_{CN}$; (d) $-E_{CO}$.

Figure 4 shows that for both XCO and XCN, and within the framework of this LCAO–MO method, the CO and CN bond orders are good indicators of not only the covalent binding energies but also the total binding energies. Discrepancies are to be noted for CN^- and CO^- (the latter is included for comparison with CN^-) in that the total binding energies for these two are less negative than needed for them to adhere to the relationships established by the other members of the two series. That these deviations are a result of "excess," in a relative sense, repulsion energies is immediately apparent from Table X. The disparities can be traced further to the $P_{AA}P_{BB}\gamma_{AB}$ contribution to the "ionic" terms of both compounds. These are the only two molecules in the two series carrying negative atom charges on both carbon and oxygen (nitrogen). Other features apparent from Table X are (1) the covalent energy term dominates the sum of core repulsion and "ionic" terms (each of these individually are larger than the covalent term; they have magnitudes on the order of 10 au) and (2) but for CN^- and CO^-, a trend of decreasing magnitude of repulsion with decreas-

Table X. Components of E_{AB}

	$-E_{AB}$(cov), au	E_{AB}(core) + E_{AB}(ion), au
HCO^+	2.93	0.88
CO	2.82	0.83
CH_3CO^+	2.84	0.90
BH_3CO	2.72	0.80
COH^+	2.60	0.83
CO^-	2.47	0.93
HCO^*	2.40	0.66
OCO	2.41	0.68
H_2CO	2.20	0.53
NCO^-	1.90	0.48
HCN	3.01	0.77
CH_3CN	2.94	0.76
CH_3NC	2.86	0.78
CN^-	3.00	0.91
OCN^-	2.74	0.69
NCN^{2-}	2.32	0.57

ing covalent energy is computed. The reader will recall that the earlier attempt of a correlation of CN force constant with binding energy met with success but that CN^- does not fit the force constant–bond order relation for XCN in that the bond order is too large; it is now seen that the CN bond order of cyanide does consistently index the covalent binding energy of cyanide but cannot properly reflect the "ionic" and core repulsion contributions to the total binding energy which would, of course, be accounted for in the force constant.

As noted in the introductory section, the relative importance of σ and π bonding changes for substitution of CN^- and CO are of current interest. Previous work[1,20] has emphasized the importance of changes in in σ binding of CN, and these computations were performed to help determine the importance of diatom σ binding in the coordination of CO and to also give an independent check of the earlier calculations for the XCN series. The P_{AB} values of Tables I and VI indicate increases in CN and CO σ binding upon carbon substitution. The σ and π contributions to the covalent binding energies are collected with the corresponding bond orders in Table XI where it is seen that the CN and CO σ and π bond orders agree with the corresponding covalent energies except for strongly back-bonding subsitutents. For CO the ratio of binding energy change:bond order change is a little smaller (0.7 au) for σ than (0.9 au) for π. The CN bond order of CH_3NC is misleadingly small. Both σ and π covalent energies of carbon monoxide and the σ covalent energy of cyanide are found to increase on protonation of the respective parents. An important factor in the case of cyanide coordination, which is apparent from consideration of E_{AB} (and which was not considered in the analyses of the earlier SCP calculations), is the parent atom repulsion which is appreciably reduced by the approach of a substituent. Within the framwork of the CNDO scheme, the decrease in CN repulsion upon coordination (*ca.* 0.1 au) is easily greater than the increase in σ covalent energy (*ca.* 0.02 au) for those XCN which exhibit an increase. Experimental evidence which can be interpreted in this way (but also in terms of σ and π bond strengthening) comes from the work of Jones who notes[20] a definite correlation between CN force constant and metal ion effective nuclear charge in octahedral cyano complex ions in which the metal ion has a few or no t_{2g} electrons. Hence these computations are in qualitative agreement with the earlier ones[1] concerning the change in CN σ energy on substitution (both sets indicate σ energy increases on the order of 0.01 and 0.03 au), but the more complete atom pair energy expression used here directs our attention to a greater importance of atom repulsion changes for any one of the processes $CN^- \rightarrow XCN$. Within a series of carbon-substituted cyano compounds, however, it appears that the variation in CN repulsion energy is generally subordinate to the total covalent energy change. A marked point of consistency between the CNDO results given here and the analyses of the SCP calculations used before[1c] is that changes in CN binding and force constant across a series of *substituted* cyano compounds are due as much, if not more, to changes in CN π binding as to changes in σ binding. According to the SCP results, the σ and π changes act in concert, decreasing CN σ binding being accompanied by decreasing CN π binding.[1c] This agreement is particularly significant since the use, in the SCP method, of the Mulliken–Wolfsberg–Hemholz approximation, with a single value of $K = 1.75$, for all off-diagonal elements of the Hamiltonian matrix has been criticized[21] for leading to underestimation of π binding relative to σ. Apparently, however, the CNDO method is not completely free of an inverse criticism. Palke and Lipscomb[22] have published the SCF Hamiltonian matrix of HCN, and we have compared this with the CNDO matrix. Following are the SCF matrix elements with the CNDO elements (au) in parentheses: C_{2s}–N_{2s} = −1.035 (−0.875); C_{2s}–N_{2p} = 0.793 (0.801); C_{2p}–N_{2s} = −1.022 (−0.942); C_{2p}–N_{2p} = 0.391 (0.619); and C_π–N_π = −0.413 (−0.715). On the whole, the σ AO elements are neither over nor underestimated, but the CNDO π elements are considerably larger than the SCF values. We can therefore expect magnified π, relative to σ, CN (and presumably CO) binding effects from the CNDO calculations. We feel cautious about putting too much emphasis on the appreciably greater magnitudes of some of the π than σ covalent energy changes in Table XI.

Table XI. XCN and XCO σ and π Bond Orders and Covalent Binding Energies

	P_σ	$-E_\sigma$(cov), au	P_π	$-E_\pi$(cov), au
HCN	1.97	1.58	2.00	1.43
CH_3CN	1.97	1.57	1.94	1.37
CH_3NC	1.89	1.57	1.86	1.29
CN^-	1.95	1.56	1.98	1.44
OCN^-	1.96	1.55	1.76	1.19
NCN^{2-}	1.94	1.49	1.40	0.83
HCO^+	1.95	1.62	1.89	1.31
CO	1.87	1.57	1.82	1.25
CH_3CO^+	1.95	1.64	1.74	1.20
BH_3CO	1.93	1.60	1.68	1.12
COH^+	1.79	1.52	1.63	1.08
HCO^*	1.94	1.55	1.41	0.85
OCO	1.94	1.58	1.36	0.83
H_2CO	1.91	1.48	1.25	0.72
NCO^-	1.92	1.45	0.92	0.45

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Summary

The CNDO calculations of XCO and XCN indicate that the currently observed CN force constant increase on CN^- coordination is primarily a result of reduced C–N repulsion *via* charge withdrawal from carbon. For the comparison CO → XCO, however, the covalent binding energy change is primarily responsible for the change in CO force constant. For moderately back-bonding substituents, the parent σ and π binding changes, as measured by bond orders and diatom binding energies, are of comparable importance. Generally speaking, *within* either series of "adducts," variation in CN and CO binding energy seems to be primarily a result of changes in C–N and C–O π binding, although the CNDO method appears to overestimate the importance of π changes, and this prevents us from placing the importance of σ changes in a completely subjugated position relative to the π changes. That both CN and CO do tend to have increased σ bond orders as a result of coordination has been traced to polarization of the nitrogen and oxygen lone-pair electrons.

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Diboranes Derived from the Hydroboration of 1,3-Butadiene. Structures, Hydrogen-Bridge Cleavage Reactions, and Factors Which Affect the Course of Bridge Cleavage

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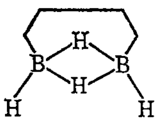
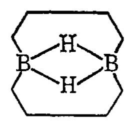
Abstract: Convenient syntheses of 1,2-tetramethylenediborane(6) (I) and 1,2-bis(tetramethylene)diborane(6) (II) have been developed. It has been possible to distinguish between II and 1,1-tetramethylene-2,2-tetramethylenediborane(6) (III) and show that II is the product prepared in the synthetic procedures employed. Ammonia and methylamines react with I and II to produce either symmetrical or unsymmetrical cleavage of the hydrogen-bridge system, with the unsymmetrical cleavage products being zwitterions. The type of cleavage product formed (identified by boron-11 nmr) depends upon the reactants. Factors which affect the course of cleavage are considered and discussed.

In recent years studies of cleavage reactions of the hydrogen-bridge system of diborane(6) by Lewis bases have suggested that unsymmetrical cleavage occurs more frequently than was previously thought.[1-5] These studies have also suggested that steric requirements of the base can influence the course of bridge cleavage reactions. With increasing methyl substitution in the methylamine series, the tendency for the base to produce symmetrical cleavage increases.[2,5]

In the present study, we have attempted to obtain additional information which could be related to the role of steric factors in determining the course of hydrogen-bridge cleavage. To this end, we have been interested in the type of cleavage product produced by a given base as substitution of the terminal positions of diborane(6) is increased. Since Moews and Parry[4] have shown that tetramethyldiborane(6) is cleaved unsymmetrically by ammonia, it would have been of interest to have determined the type of cleavage produced by methyl-substituted amines on the series of methyl-substituted diboranes. However, because of the tendency of methyldiboranes to rearrange,[6] it was decided to work with other substituted diboranes. The compounds 1,2-tetramethylenediborane(6) (I) and 1,2-bis(tetramethylene)diborane(6) (II) were chosen.

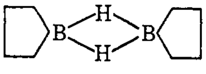


I



II

They have been prepared from the hydroboration of 1,3-butadiene and show no tendency to rearrange. However, their structures have been the subject of some debate. While boron-11 nmr spectroscopy has clearly established structure I,[7] there is no simple spectroscopic approach which will distinguish between structure II and an alternative structure III, 1,1-tetramethylene-2,2-tetramethylenediborane(6).



III

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[1] G. E. McAchran and S. G. Shore, *Inorg. Chem.*, 4, 125 (1965).

[2] S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, 87, 2755 (1965). References to the earlier work of Parry, Schultz, and Shore which established the first example of unsymmetrical cleavage, $BH_2(NH_3)_2{}^+BH_4{}^-$, are given here.

[3] O. T. Beachley, *Inorg. Chem.*, 4, 1823 (1965).

[4] P. C. Moews, Jr., and R. W. Parry, *ibid.*, 5, 1552 (1966).

[5] M. Inoue and G. Kodama, *ibid.*, 7, 430 (1968).

[6] H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, 57, 621 (1935); H. I. Schlesinger, L. Horwitz, and A. B. Burg, *ibid.*, 58, 407 (1936).

[7] H. G. Weiss, W. J. Lehmann, and I. Shapiro, *ibid.*, 84, 3840 (1962); H. H. Lindner and T. Onak, *ibid.*, 88, 1886 (1966).