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Carbonyl Boron and Related Systems: An ab Initio Study of B−X and YB≡BY ($^1\Sigma_g{}^+$), Where X = He, Ne, Ar, Kr, CO, CS, N_2 and Y = Ar, Kr, CO, CS, N_2

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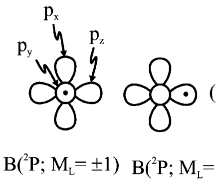
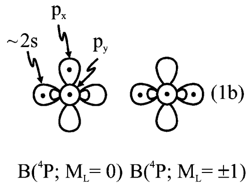
Using the coupled-cluster methodology and large correlation consistent basis sets, we have examined the BX and YBBY ($^1\Sigma_g{}^+$) molecules, where X = He, Ne, Ar, Kr, CO, CS, and N_2 and Y = Ar, Kr, CO, CS, and N_2. For the B−X series we have constructed full potential energy curves reporting total energies, equilibrium geometries, binding energies, and also spectroscopic constants for the diatomic sequence. The B−CO, B−CS, and B−N_2 ground states are of $^4\Sigma^-$ and $^2\Pi$ symmetries, respectively, with the $^4\Sigma^-$ states having remarkably strong binding energies with respect to their adiabatic fragments. For all the triatomics the first excited ^4P state of B plays an instrumental role in the binding process, while the bonding mechanism in either the $^2\Pi$ or $^4\Sigma^-$ symmetries is due to charge transfer to the empty $2p_z$ orbital of the B atom. The YBBY series results by singlet coupling two B−Y $^4\Sigma^-$ moieties, leading to acetylene-like YB≡BY systems of $^1\Sigma_g{}^+$ symmetry.

Introduction

There is little doubt that one of the most fascinating elements of the periodic table is boron.[1] It is the only nonmetal in Group 13 (IIIA) of the periodic table and shows marked similarities to its neighbor, carbon, and its relative, silicon.[2] Its ability to form stable covalent molecules with a variety of elements or polynuclear materials with bewildering geometries is really staggering.[1,2] This ability can be traced to its unique ground $^2P(2s^22p^1)$ and first excited $^4P(2s^12p^2)$ state, located 3.579 eV (= 82.53 kcal/mol) higher.[3] The examination of the valence bond Lewis (vbL) diagrams of these atomic states is helpful in understanding boron's versatility in bonding.

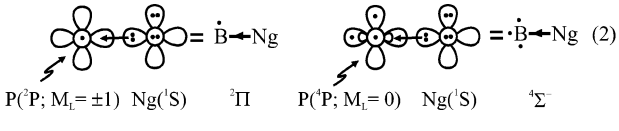


(1a),



(1b)

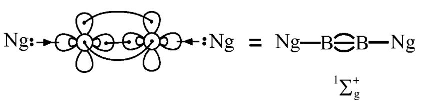
The above diagrams clearly suggest that by properly exploiting the valence orbital vacancies, a variety of potentially stable and exotic molecular systems is plausible (vide infra). In particular, any closed-shell species can form, in principle, dative (harpoon-like) bonds by transferring electron density to the p_π or p_σ orbitals of the B atom. Take for example a noble gas (Ng) atom in its ground state (^1S), attacking either the ^2P or the ^4P state of boron. Apart from repulsive or van der Waals interactions, nothing much is expected to happen in the case of $M_L = 0$ (^2P) and $M_L = \pm1$ (^4P) components. However, the situation is entirely different if one considers the $M_L = \pm1$ (^2P) or $M_L = 0$ (^4P) components. Using vbL icons, we find that the following two molecular states are possible for any Ng.



(2)

In addition, the $^4\Sigma^-$ states are predicted in general to be much more stable in comparison to the $^2\Pi$ states, because of the $2s^22p^1$ (^2P) → $2s^12p^2$ (^4P) "opening" resulting in the ability of a lone pair of any appropriate ligand (or a Lewis basis, :L) to "feel" the attraction of the semi-exposed 1s core of the B atom.

Now, bringing together the two $^4\Sigma^-$ $\cdot\dot{\underset{\cdot}{B}} \leftarrow$ Ng (or for that matter $\cdot\dot{\underset{\cdot}{B}} \leftarrow$ L) fragments and coupling the two quartets into a singlet, we can form the NgBBNg linear singlets



(3)

The similarity of the $^1\Sigma_g{}^+$ (or $^1\Sigma^+$ if the two outside ligands are different) state with acetylene or acetylene-like compounds is striking. This is natural, however, if one realizes that the B ^2P ($M_L = \pm1$) and ^4P ($M_L = 0$) states are isovalent to the $X^2\Pi$ and $a^4\Sigma^-$ states of CH, respectively, with the latter being 17.2 kcal/mol higher.[4] Of course, the $^4\Sigma^-$ state of CH (originating from the ^5S atomic state of carbon), is responsible for the formation of acetylene by spin coupling two $^4\Sigma^-$ states into a singlet, $^1\Sigma_g{}^+$. It is useful at this point to recall that the C−H $^4\Sigma^-$ binding energy is $D_e = 66.2$ kcal/mol,[4] as contrasted to the remarkably high binding energy of C−H in the acetylene molecule, D_0 (HCC−H) = 131.5 kcal/mol.[5] In analogy, the LBB−L binding energy is expected to be higher than the D_e in the corresponding $^4\Sigma^-$ molecules (L = Ng or otherwise, see below).

Our high level coupled cluster RCCSD(T) computations completely support the above considerations. We presently report on the $^4\Sigma^-$ B−Ng (Ng = He, Ne, Ar, Kr) diatomics and the two symmetric $^1\Sigma_g{}^+$ tetratomics ArBBAr and KrBBKr. What is really very interesting is that both tetratomics are stable enough to be isolable under the proviso that they do not decay to a lower singlet surface, for instance, B_2[(1) or (2) $^1\Sigma_g{}^+$] + 2 Kr(^1S) (but see below).

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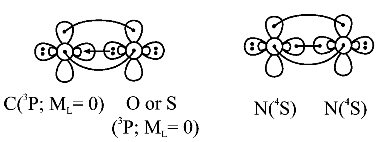
As was already mentioned, any closed-shell Lewis base :L can, in principle, form stable B−L (doublets or quartets) and the corresponding LBBL (or LBBL′) singlets. Here we also consider three isovalent Lewis bases, namely, L = CO ($X^1\Sigma^+$), CS ($X^1\Sigma^+$), and $N_2(X^1\Sigma_g^+)$, whose vbL diagrams are:



(4)

Clearly, and according to structures 2 and 3, the formation of the linear $^2\Pi$ or $^4\Sigma^-$ triatomics B−CO (B−OC), B−CS (B−SC), and B−N_2 and the acetylene-like $^1\Sigma_g^+$ hexatomics OC−BB−CO, SC−BB−CS, and N_2−BB−N_2 is easily understood. As a matter of fact, it is expected that the dissociation energy (D_e) of B−L is larger in the $^4\Sigma^-$ rather than in the $^2\Pi$ state and increases along the series B−N_2, B−CO, and B−CS according to the Lewis "basicity" (or dipole moment) of N_2, CO, and CS. It is also expected that the LBB−L binding energies are larger than the corresponding D_e's in the $^4\Sigma^-$ B−L triatomics.

Experimentally, the BCO molecule was observed for the first time in solid neon and argon matrixes at 4 K by Hamrick et al.[6] These workers recorded its ESR spectrum and concluded that the ground state of BCO is of $^4\Sigma^+$ symmetry, with three parallel spins located mainly on the B atom. Subsequent calculations at the UHF-SCF and MBPT(2)/DZP level[6] confirmed the above results, indicating also that the ground state is a quartet, with the $^2\Pi$ state located 118.7 kcal/mol higher at the SCF level. It was also found that the B−CO isomer is favored by 73.5 and 67.7 kcal/mol at the MBPT(2) and CCSD+T(CCSD) levels, respectively, as compared to B−OC. Burkholder and Andrews,[7] using matrix infrared spectra, observed the BCO, $(BCO)_2$, and $B(CO)_2$ species. Their theoretical results at the MBPT(2)/DZP level also showed that the ground state of BCO is a quartet with a B−CO binding energy of 24.0 kcal/mol and that the linear $(BCO)_2$ dimer is by 52 kcal/mol more stable than two separate BCO molecules.

No useful conclusions can be drawn from the ab initio MP2/6-31G* calculations of Skancke and Liebman[8] on BCO published in 1994.

In 2002, Zhou et al.,[9] using matrix isolation infrared absorption spectroscopy, inferred the existence of the linear $OC^{11}B^{11}BCO$ molecule. In addition, employing also CAS(4,4)/6-311+G(d) and (U)B3LYP/6-311+G(d) calculations, they concluded that OCBBCO has an acetylenic structure, O≡C−B≡B−C≡O, which as they say, "satisfies the octet rule" (see also refs 10 and 11 and references therein).

Presently, for the diatomics B−Ng (Ng = He, Ne, Ar, Kr) and the triatomics B−CO, B−CS, and B−NN, we report full PECs, geometries, and binding energies, as well as the usual spectroscopic constants for the B−Ng series, using the coupled cluster method and large basis sets. The fact that we can obtain full potential energy curves through a single reference method, or even at the Hartree−Fock level, testifies to the correctness of the bonding mechanism proposed. We also examine systematically the linear polyatomics LBBL ($^1\Sigma_g^+$), where L = Ar, Kr, CO, CS, and N_2, reporting geometries and binding energies.

Methodology

For the B−L ($^2\Pi$, $^4\Sigma^-$) diatomics and triatomics (L = Ng, CO, CS, N_2), the augmented correlation consistent basis sets of quintuple quality, aug-cc-pV5Z (= A5Z), of Dunning and co-workers were used, generally contracted, while for the LBBL ($^1\Sigma_g^+$) series (L = Ar, Kr, CO, CS, and N_2) the plain cc-pVQZ (= QZ) basis set was employed contracted in a similar fashion.[12] The single reference restricted coupled cluster singles and doubles with perturbative triples method, RCCSD(T), was employed for all molecules studied. For the open-shell systems, RCCSD(T) is based on restricted open-shell Hartree−Fock orbitals plus certain restrictions on the CC amplitudes to make the linear part of the wave function a spin eigenfunction.[13] Only "valence" electrons were correlated, i.e., the ∼1s (B, C, N, O, Ne), ∼1s2s2p (S, Ar), and ∼1s2s2p3s3p3d (Kr) orbitals were kept always doubly occupied. Dipole moments of the diatomics and triatomics were computed by the finite field method using field strengths of about 5×10^{-5} to 5×10^{-4} au. To keep our calculations manageable, geometric optimizations of all polyatomics were done via a point-energy grid.

All our calculations were performed with the MOLPRO 2002 program.[14]

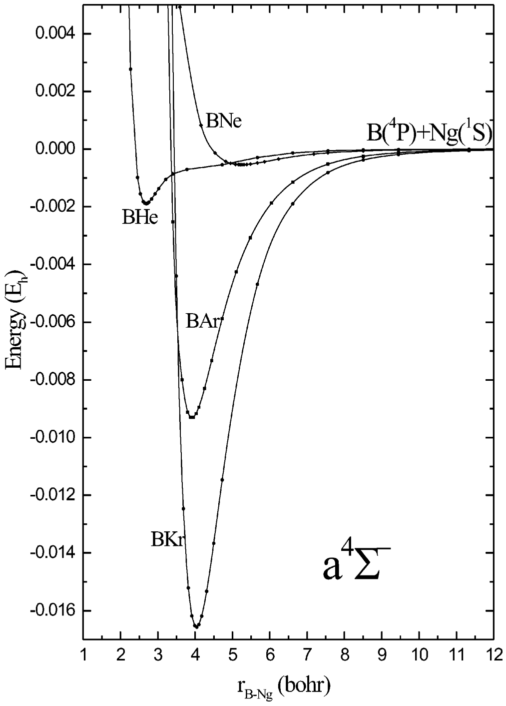


Figure 1. Potential energy curves of the $^4\Sigma^-$ B−Ng series, Ng = He, Ne, Ar, Kr. RCCSD(T)/A5Z level.

Results and Discussion

Figure 1 depicts potential energy curves (PEC) of the $^4\Sigma^-$ B−Ng (Ng = He, Ne, Ar, Kr) series, while Figures 3−5 show $^2\Pi$ and $^4\Sigma^-$ PECs of the triatomics B−CO, B−CS, and B−NN, respectively. Tables 1−3 list all our pertinent numerical results. From the previous discussion it is clear that the energy separation B ($^4P \leftarrow {}^2P$) plays a significant role for the reliable prediction of the energetics of these systems. At the RCCSD(T) level, this energy splitting is predicted to be 3.586 (A5Z) and 3.579 (QZ) eV, as compared to the experimental value of 3.579 eV.[3]

We discuss first the B−Ng diatomics, followed by the triatomics, and finally the acetylene-like LBBL polyatomics.

(a) B−Ng, Ng = He, Ne, Ar, Kr. We have not examined the B−Ng ground $X^2\Pi$ or $^2\Sigma^+$ states stemming from the B ^2P-

TABLE 1: Total Energies *E* (hartree), Bond Distances r_e (Å), Dissociation Energies D_e (kcal/mol), Harmonic and Anharmonic Frequencies ω_e and $\omega_e x_e$ (cm^{-1}), Rotation−Vibration Coupling Constants α_e (cm^{-1}), Dipole Moments μ (Debye), and Total Charge on B q_B (e$^-$), of the B−Ng a$^4\Sigma^-$ Series, Ng = He, Ne, Ar, Kr. RCCSD(T)/A5Z Level of Theory

species	$-E$	r_e	$D_e{}^a$	$\omega_e{}^b/\omega_e{}^c$	$\omega_e x_e{}^b/\omega_e x_e{}^c$	$\alpha_e{}^b/\alpha_e{}^c$	μ^d	$q_B{}^e$
B−He	27.374790	1.4213	1.18	−[f]	−	−	1.209	−0.09
B−Ne	153.330080	2.7707	0.34	58.3/60.3	7.8/8.4	0.036/0.037	0.123	−0.002
B−Ar	551.562462	2.0709	5.85	286/297	11.3/12.2	0.017/0.019	2.162	−0.16
B−Kr	2776.76713	2.1361	10.40	350/365	8.7/9.4	0.009/0.010	2.655	−0.31

[a] D_e's with respect to B(^{4}P) + Ng(^{1}S). [b] ^{11}B−Ng, Ng = ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr. [c] ^{10}B−Ng. [d] Calculated by the finite field method. [e] Mulliken charges at the Hartree−Fock level. [f] $G(0) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8 + ... = 186$ (^{11}B−He), 188 (^{10}B−He) cm^{-1}, by solving numerically the one-dimensional rovibrational Schrödinger equation.

TABLE 2: Total Energies *E* (hartree), Equilibrium Bond Distances r_e (Å), Dissociation Energies $D_e{}^a$ (kcal/mol), Dipole Moments μ^b (Debye), Energy Separations T_e (kcal/mol) of BCO, BCS, and BNN $^2\Pi$ and $^4\Sigma^-$ States^c

BCO, $\tilde{X}^4\Sigma^-$	BCS, $\tilde{X}^4\Sigma^-$	BNN, $\tilde{X}^2\Pi$
$E = -137.832840$	$E = -460.42677$	$E = -134.018897$
$r_{B-C} = 1.421$	$r_{B-C} = 1.396$	$r_{B-N} = 1.466$
$r_{C-O} = 1.164$ (1.131^d)	$r_{C-S} = 1.565$ (1.540^d)	$R_{N-N} = 1.149$
$D_{B-CO} = 102.8$	$D_{B-CS} = 141.8$	$D_{B-N_2} = 1.19$
$\mu = 0.591$	$\mu = 0.121$	$\mu = -1.43$
BCO, $\tilde{a}^2\Pi$	BCS, $\tilde{a}^2\Pi$	BNN, $\tilde{a}^4\Sigma^-$
$E = -137.821976$	$E = -460.41270$	$E = -134.006543$
$r_{B-C} = 1.602$	$r_{B-C} = 1.541$	$r_{B-N} = 1.323$
$r_{C-O} = 1.153$	$r_{C-S} = 1.545$	$R_{N-N} = 1.176$ (1.100^d)
$D_{B-CO} = 13.3$	$D_{B-CS} = 50.4$	$D_{B-N_2} = 76.1$
$\mu = -1.48$	$\mu = -3.32$	$\mu = 1.39$
$T_e = 6.82$	$T_e = 8.83$	$T_e = 7.75$

[a] With respect to adiabatic products. [b] Calculated by the finite field method. [c] RCCSD(T)/A5Z level of theory. [d] r_e of the free CO(X$^1\Sigma^+$), CS(X$^1\Sigma^+$), and N$_2$(X$^1\Sigma_g{}^+$) molecules at the RCCSD(T)/A5Z level. Experimental values are 1.1283, 1.535, and 1.0996 Å, respectively; ref 18.

(M$_L$ = ±1,0) state (structures 1a and 2) with the understanding that they are either repulsive or weakly bound.[15] For the $^4\Sigma^-$ states correlating to B (^{4}P, M$_L$ = 0) + Ng (^{1}S) (structure 2), moving from Ne to Ar and next to Kr, the binding energy increases "regularly" from 0.34 to 5.85 to 10.40 kcal/mol (Table 1). The word "regularly" refers to Figure 2; by plotting D_e's vs the (experimental) static polarizabilities α (Å^3) of Ne (0.395), Ar(1.6411), and Kr(2.48),[16] a straight line is obtained (Figure 2). Extrapolating to the polarizability of Xe (4.04), the binding energy of the $^4\Sigma^-$ state of B−Xe can be estimated, $D \cong 18$ kcal/mol. The situation in the B−He case is different; the exceptionally small atomic radius of the He atom (the smallest of all elements) and its lack of p$_\pi$ electrons allow a very close approach to the B atom, resulting in an "anomalous" high binding energy, D_e = 1.18 kcal/mol, despite its small polarizability, α = 0.205 Å^3. As expected, the B−He bond distance is by far the smallest of all B−Ng diatomics. It is interesting that the morphology of the B−Ng D_e plot as a function of the polarizabilities α is similar to the corresponding Li−Ng plot (Ng = He, Ne, Ar, Kr) A$^2\Pi$ series where an Ng atom binds to the first excited ^{2}P state of the Li atom, of course with an identical mechanism.[17] Another interesting feature of the B−Ng $^4\Sigma^-$ interaction is the substantial charge transfer from the Ng atoms to the 2p$_z$ orbital of the B atom. Notwithstanding the

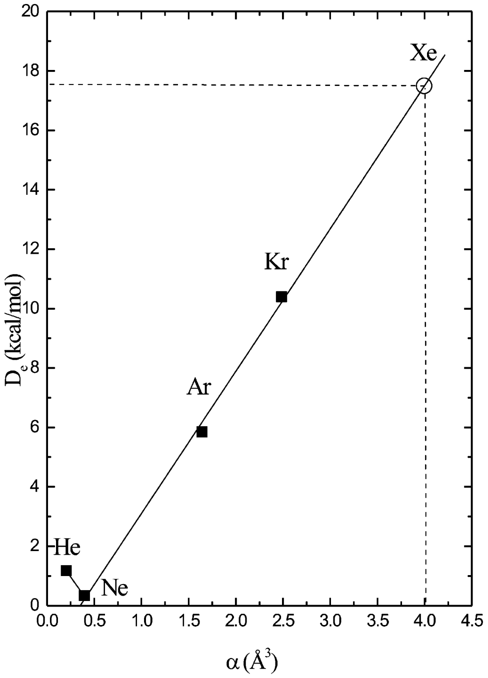


Figure 2. Plot of the $^4\Sigma^-$ B−Ng binding energies vs the Ng experimental polarizabilities α(Å^3). Ng = He, Ne, Ar, and Kr.

TABLE 3: Total Energies *E* (hartree), Geometries r_e (Å), Binding Energies D_e (kcal/mol), and Charge Distributions q (e$^-$)^a of the ArBBAr, KrBBKr, OCBBCO, SCBBCS, and NNBBNN $^1\Sigma_g{}^+$ States at the RCCSD(T)/QZ Level

Ar−B≡B−Ar	Kr−B≡B−Kr	OC−B≡B−CO	SC−B≡B−CS	NN−B≡B−NN
$E = -1103.35604$	$E = -5553.77114$	$E = -275.87310$	$E = -921.04861$	$E = -268.21825$
$r_{B-Ar} = 1.879$	$r_{B-Kr} = 1.999$	$r_{B-C} = 1.456$	$r_{B-C} = 1.421$	$r_{B-N} = 1.357$
$r_{B-B} = 1.394$	$r_{B-B} = 1.400$	$r_{B-B} = 1.439$	$r_{B-B} = 1.482$	$r_{B-B} = 1.460$
$D_{B-Ar} = 46.5^b$	$D_{B-Kr} = 57.6^d$	$r_{C-O} = 1.154$	$r_{C-S} = 1.555$	$R_{N-N} = 1.138$
$D_{B-B} = 160.1^c$	$D_{B-B} = 161.8^e$	$D_{B-CO} = 226.6^f$	$D_{B-CS} = 295.6^h$	$D_{B-N_2} = 171.5^j$
$q_B = -0.30$	$q_B = -0.39$	$D_{B-B} = 146.3^g$	$D_{B-B} = 137.5^i$	$D_{B-B} = 144.1^k$
		$q_B = -0.24$	$q_B = -0.06$	$q_B = -0.13$
		$q_C = +0.48$	$q_C = -0.02$	$q_{N_1} = +0.05$

[a] Hartree−Fock Mulliken charges. [b] With respect to B$_2$ [(3)$^1\Sigma_g{}^+$] + 2Ar (^{1}S). [c] With respect to 2BAr (a$^4\Sigma^-$). [d] With respect to B$_2$ [(3)$^1\Sigma_g{}^+$] + 2Kr (^{1}S). [e] With respect to 2BKr (a$^4\Sigma^-$). [f] With respect to B$_2$ [(3)$^1\Sigma_g{}^+$] + 2CO (X$^1\Sigma^+$). [g] With respect to 2BCO ($\tilde{X}^4\Sigma^-$). [h] With respect to B$_2$ [(3)$^1\Sigma_g{}^+$] + 2CS (X$^1\Sigma^+$). [i] With respect to 2BCS ($\tilde{X}^4\Sigma^-$). [j] With respect to B$_2$ [(3)$^1\Sigma_g{}^+$] + 2N$_2$ (X$^1\Sigma_g{}^+$). [k] With respect to 2BNN ($\tilde{a}^4\Sigma^-$).

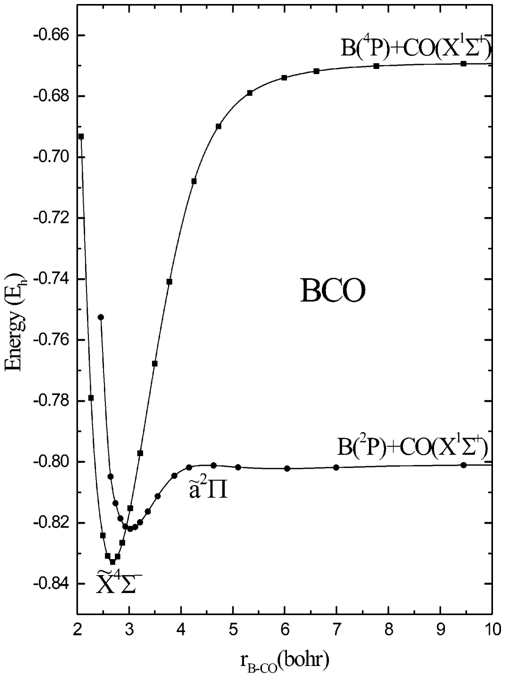


Figure 3. Potential energy curves of the $\tilde{X}^4\Sigma^-$ and $\tilde{a}^2\Pi$ states of B−CO. RCCSD(T)/A5Z level.

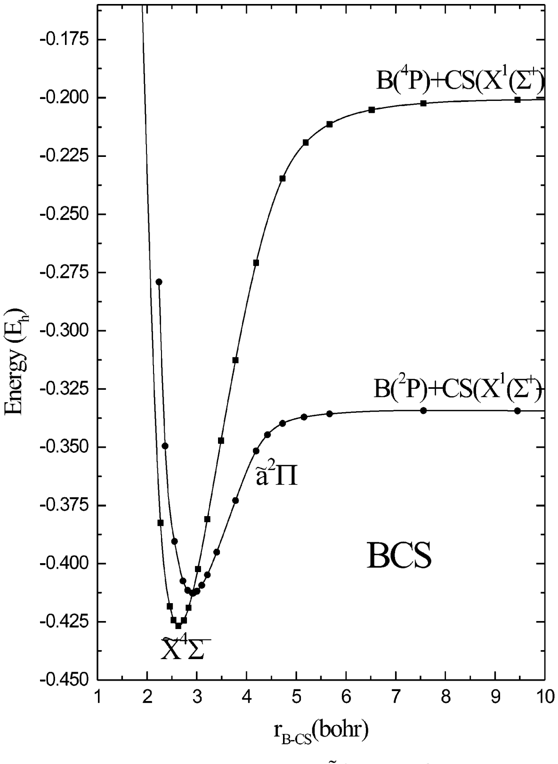


Figure 4. Potential energy curves of the $\tilde{X}^4\Sigma^-$ and $\tilde{a}^2\Pi$ states of B−CS. RCCSD(T)/A5Z level.

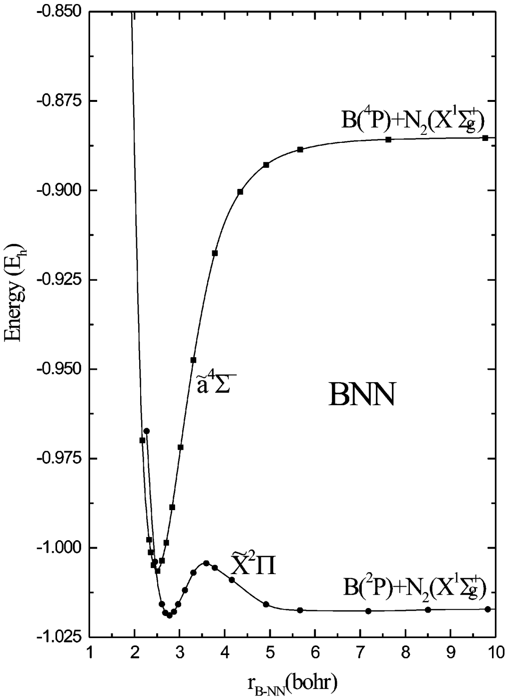
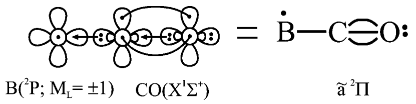


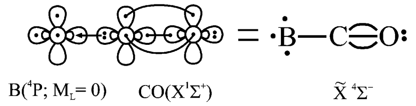
Figure 5. Potential energy curves of the $\tilde{X}^2\Pi$ and $\tilde{a}^4\Sigma^-$ states of B−NN. RCCSD(T)/A5Z level.

pitfalls of the Mulliken population analysis the trend is clear: going through a minimum in the B−Ne molecule (larger interatomic distance), the charge on B in the B−Kr species, 0.31 e$^-$, is indeed significant, giving rise also to the largest dipole moment among the B−Ng diatomics (Table 1).

(b) B−L, L = CO, CS, N$_2$. Figures 3−5 depict $^2\Pi$ and $^4\Sigma^-$ PECs of these systems correlating to B (^{2}P, M$_L$ = ±1) and B (^{4}P, M$_L$ = 0), respectively. Considering CO ($X^1\Sigma^+$) as an example, the bonding mechanism of all three species is clearly captured by the following vbL icons (see also structures 2 and 4)

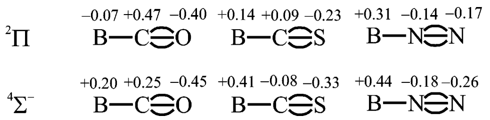


(5a)



(5b)

Structures 5a and 5b predict a strong electron transfer from L to 2p$_z$ orbital of boron, giving rise to a σ-bond, an interaction (or "conjugation" or "back-bonding") in the π-system, as well as a stronger B−L bond in the $^4\Sigma^-$ than the $^2\Pi$ states (vide supra). Indeed, Mulliken atomic charges at the Hartree−Fock level indicate that the 2p$_z$ B orbital accepts (0.76, 0.66), (0.87, 0.74), and (0.75, 0.63) electrons in the ($^2\Pi$, $^4\Sigma^-$) states of the B−CO, B−CS, and B−NN molecules, respectively. An equal or larger amount of charge, however, is transferred back to the π-system of CO, CS, and N$_2$ ligands, resulting in a rather positively charged boron atom. Total atomic Hartree−Fock Mulliken charges are indicative:

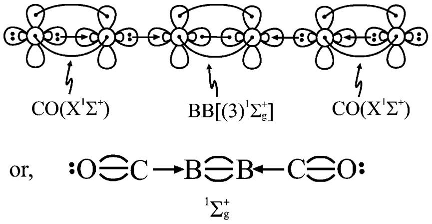


Now, what is interesting in the B−L $^4\Sigma^-$ series are the dissociation energies, which increase from 76.1 kcal/mol in the B−NN case to 102.8 kcal/mol in B−CO, and to a remarkable strong bond of 141.8 kcal/mol in the B−CS molecule (Table 2), with respect to the adiabatic products B(^{4}P) + L($X^1\Sigma^+$ or $X^1\Sigma_g{}^+$). On the contrary, D_e values of B−NN, B−CO, and B−CS in the $^2\Pi$ state are much weaker, namely, 1.19, 13.3 and 50.4 kcal/mol, respectively. The interplay between the $^4\Sigma^-$

and $^2\Pi$ binding energies and the boron $^4P \leftarrow {}^2P$ excitation energy is, of course, the reason that the ground states of BCO and BCS are of $^4\Sigma^-$ symmetry, while BNN has $^2\Pi$ ground state, with T_e ($\tilde{a}^2\Pi \leftarrow \tilde{X}^4\Sigma^-$) and T_e ($\tilde{a}^4\Sigma^- \leftarrow \tilde{X}^2\Pi$) values of 6.82, 8.83, and 7.75 kcal/mol, respectively (Table 2 and Figures 3−5).

As a final comment to this section, we would like to add that we do not have a clear explanation of the 8.1 kcal/mol hump that is observed in the BNN $\tilde{X}^2\Pi$ potential energy curve (Figure 5). From the population analysis though, it seems that the N_2 is very reluctant to transfer e^- to the empty $2p_z$ B orbital up to $r_{B-N_2} = 3.5$ bohr, the hump maximum. From 3.5 bohr on, however, and approaching the bottom of the curve, electrons are transferred copiously to the $2p_z$ orbital (0.76 e^- at r_e), creating a metastable state of 9.3 kcal/mol "binding" with respect to the maximum of the barrier.

(c) ArBBAr, KrBBKr, LBBL (L = CO, CS, N_2). Taking again as a prototype the CO ligand, a vbL diagram pertaining to all the above molecules is the following (see also structures 3 and 4)



(6)

clearly an acetylene-like description. Note that the in situ B_2 moiety is triple-bonded, meaning that B_2 finds itself in its third $(3)^1\Sigma_g^+$ ($= 2\sigma_g^2 1\pi_u^4$) state, 4.56 eV ($r_e = 1.400$ Å) above its ground $X^3\Sigma_g^-$ state at the RCCSD(T)/QZ level (see also ref 19 for the B_2 molecule).

Focusing first at the ArBBAr and KrBBKr systems, it is observed that the $^1\Sigma_g^+$ symmetry is not the global minimum of either the $B_2(X^3\Sigma_g^-) + 2Ng(^1S)$ or $B_2[(1)$ or $(2)^1\Sigma_g^+] + 2Ng(^1S)$ channels (the $(1)^1\Sigma_g^+$ state of B_2 is about 0.91 eV above the $X^3\Sigma_g^-$; ref 19), due to the "weak" ArBB−Ar, KrBB−Kr bindings (Table 3). However, a remarkable NgBB−Ng bond strengthening is noted in comparison with the B−Ar, B−Kr $^4\Sigma^-$ states (Table 1). Indeed, D_e values of the latter diatomics are 5.85 and 10.40 kcal/mol, as contrasted to mean $\bar{D}_e$ values of 23.2 and 28.8 kcal/mol of the corresponding tetratomics. Going from BAr, BKr ($^4\Sigma^-$) to ArBBAr, KrBBKr ($^1\Sigma_g^+$), a significant bond length shortening of 0.19 and 0.14 Å, respectively, is manifested with a concomitant increase of charge transfer to the $2p_z$ B orbital. In addition, the dissociation energy of NgB≡BNg → 2BNg ($^4\Sigma^-$) is 160.1 and 161.8 kcal/mol for Ng = Ar and Kr, respectively, about 36 kcal/mol stronger than the $D_e = 124.0$ kcal/mol of $B_2[(3)^1\Sigma_g^+]$ with respect to $2B(^4P)$ fragments. No significant B−B bond length change is observed from B_2 $[(3)^1\Sigma_g^+]$ to either ArB≡BAr or KrB≡BKr.

Now, the ground state of OCBBCO, SCBBCS, and NNBBNN is of $^1\Sigma_g^+$ symmetry, the result of the astonishing large mean $\bar{D}_e$ OCBB−CO, SCBB−CS, NNBB−NN bond values of 113.3, 147.8, 85.7 kcal/mol, respectively (Table 3). In comparison to the corresponding $^4\Sigma^-$ triatomics (Table 2), these values increase by 10.5, 6.0, and 9.6 kcal/mol, respectively. The dissociation energies of LB≡BL ($\tilde{X}^1\Sigma^+$) → 2BL ($^4\Sigma^-$), L = CO, CS, N_2, of 146.3, 136.3, 144.1 kcal/mol, respectively, show an increase of about 20 kcal/mol (L = CO, N_2) and 14 kcal/mol (L = CS) as compared to the $D_e = 124.0$ kcal/mol of $B_2[(3)^1\Sigma_g^+]$ with respect to $2B(^4P)$ fragments at the same level of theory, approximately twice as small as in the Ar, Kr cases. Concomitantly, a B−B bond lengthening is observed of 0.04, 0.08, and 0.06 Å as we move from OCBBCO to SCBBCS to N_2BBN_2, respectively, as compared to the diatomic $B_2[(3)^1\Sigma_g^+]$, the result of the p_π-conjugation shown in structure 6 and absent in the Ar, Kr substituents.

As a final remark we would like to add that the SCBBCS and N_2BBN_2 molecules being ground-state singlets should be isolable, and perhaps the same is true for their Ng companions, although the latter are not global minima. The OCBBCO species was observed more than 10 years ago by Burkholder and Andrews[7] (see also refs 9 and 11).

Conclusions

Employing the coupled cluster approach RCCSD(T), in conjunction with quadruple and augmented quintuple correlation consistent basis sets, we have explored the bonding nature of the sequence of molecules B−Ng($^4\Sigma^-$), Ng = He, Ne, Ar, and Kr; the $^4\Sigma^-$ and $^2\Pi$ states of BCO, BCS, and BN_2; and the $^1\Sigma_g^+$ states of the acetylene-like polyatomics ArB≡BAr, KrB≡BKr, OCB≡BCO, SCB≡BCS, and N_2B≡BN_2. At the RCCSD(T)/A5Z level, full potential energy curves have been constructed for the B−Ng ($^4\Sigma^-$) diatomics and for both $^4\Sigma^-$ and $^2\Pi$ states of the triatomics.

For all molecules studied, we report total energies, geometries, dissociation energies, and spectroscopic constants for the B−Ng sequence. It is interesting that all the B−Ng $^4\Sigma^-$ species are bound with respect to $B(^4P) + Ng(^1S)$, therefore potentially observable, the largest $D_e = 10.40$ kcal/mol being that of B−Kr. The ground states of BCO($\tilde{X}^4\Sigma^-$), BCS($\tilde{X}^4\Sigma^-$), and $BN_2(\tilde{X}^2\Pi)$ have binding energies of 102.8, 141.8, and 1.19 kcal/mol, respectively, with respect to $B(^4P) + CO(X^1\Sigma^+)$, $CS(X^1\Sigma^+)$, and $B(^2P) + N_2(X^1\Sigma_g^+)$; however, the $\tilde{a}^4\Sigma^-$ state of BN_2, 8 kcal/mol above the $\tilde{X}^2\Pi$, has a $D_e = 76.1$ kcal/mol with respect to $B(^4P) + N_2(X^1\Sigma_g^+)$.

Although it was not mentioned in the Results and Discussion section, we have also examined at the RCCSD(T)/A5Z level the $^2\Pi$ and $^4\Sigma^-$ states of the isomers B−OC and B−SC. For both systems the ground state ($\tilde{X}^2\Pi$) is repulsive, while the $\tilde{a}^4\Sigma^-$ state is bound with respect to $B(^4P) + CO(X^1\Sigma^+)$ or $CS(X^1\Sigma^+)$ by 34.3 and 59.6 kcal/mol respectively, with r_e(B−OC) = 1.325, r_e(BO−C) = 1.232 Å and r_e(B−SC) = 1.672, r_e(BS−C) = 1.637 Å. The $\tilde{X}^4\Sigma^-$ states of BCO and BCS are 68.5 and 82.1 kcal/mol lower than the $\tilde{a}^4\Sigma^-$ states of BOC and BSC, respectively.

The binding mechanism in all the above systems, particularly in the most interesting $^4\Sigma^-$ state, is a dative bond caused by charge transfer from the ligand L to the empty $2p_z$ orbital of the B $^4P(M_L = 0)$ state. Therefore, it is understood that any Lewis "base", for instance NH_3, OH_2, etc., is capable, in principle, of forming stable quartet states of the type $\cdot\overset{\cdot}{\underset{\cdot}{B}} \leftarrow :L$.

The coupling of the two B−L quartets into a singlet ($X^1\Sigma_g^+$) gives rise to the acetylene-like LB≡BL molecules with the in situ B_2 in its $(3)^1\Sigma_g^+$ excited state. The characteristic of all those systems is the remarkable strengthening of the L−BB−L bonds, as compared to the B−L of the corresponding $^4\Sigma^-$ states.

A final comment is in order. From the previous discussion it is obvious that we can envisage a tremendous variety of BL and LBBL or LBBL′ (L′ ≠ L) molecular systems, where L is any appropriate ligand. In particular, referring to structure 6 but with L = N_2 instead of CO for instance, the formation of a linear (or not) conjugate "polymeric" system of the form ···NN−B≡B−NN−B≡B−NN−B≡B−NN··· is clearly possible, with, perhaps, unusual and fascinating material properties.

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