First-Principles Investigation of the Boron and Aluminum Carbides BC and AlC and Their Anions BC- and AlC-. 1

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First-Principles Investigation of the Boron and Aluminum Carbides BC and AlC and Their Anions BC^- and AlC^-. 1

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Using ab initio multireference methods and large correlation consistent basis sets, we have investigated the ground electronic structure of the carbides BC and AlC, the ground and the first two excited states of the corresponding anions, BC^- and AlC^-, and the ground (linear) structures of the hydrides H−BC and H−AlC. By employing a series of increasing size basis sets for the BC molecule, i.e., cc-pV*n*Z, aug-cc-pV*n*Z, cc-pCV*n*Z, and aug-cc-pCV*n*Z, $n = 2$, 3, 4, and 5, we have examined the convergence of its properties as a function of *n*. For both the neutral diatomic species and their anions we have obtained full potential energy curves, bond distances (r_e), dissociation energies (D_e), and the usual spectroscopic constants. For the BC molecule, our best r_e and D_e values are $r_e = 1.4911$ Å and $D_e = 102.2$ kcal/mol in excellent agreement with experimental results. In the AlC case the calculated $D_e = 77.13$ kcal/mol is at least 12 kcal/mol higher than the experimental number. No experimental or theoretical data exist in the literature for the anion BC^-. For this system we obtain $r_e = 1.4445$ Å and $D_e = 118.67$ kcal/mol; the corresponding values of the AlC^- species are $r_e = 1.8945$ Å and $D_e = 77.16$ kcal/mol.

1. Introduction

With the purpose of understanding the bonding, as well as to obtain accurate spectroscopic parameters of the diatomic carbides BC and AlC, we have performed multireference ab initio calculations using large to very large basis sets. Without doubt, ZC (solid) carbides, Z = B, Al, are a very interesting class of materials.[1] Nevertheless, the basic diatomic species do not seem to have attracted the wider attention of the scientific community. It is characteristic that in the very well-known book on diatomics by Huber and Herzberg[2] there is no information on the AlC molecule, and as far as the BC molecule is concerned, the only piece of experimental information given is its dissociation energy. The scarcity of experimental data, in particular, is rather due to the difficulty of creating and uniquely identifying these carbides as “single” molecular entities.

The simple diatomic BC was first observed by Verhaegen et al. in 1964,[3] who also determined its dissociating energy. In 1989 the first spectroscopic study by electron spin resonance[4] confirms that the ground BC state is $X^4\Sigma^-$ in accord with earlier theoretical predictions. Table 1 collects all existing data, theoretical[4−10] and experimental,[1,3,11] concerning the BC ground state. It is fair to mention that Kouba and Öhrn[5] as early as 1970, employing a minimal Slater basis and a natural orbital CI approach, identified correctly the ground and the qualitative ordering of a few excited states, among a total of 54 calculated states.

Table 2 lists theoretical[6,12−14] and experimental[15−17] data on the ground state of AlC. The molecule was first observed in 1990 by Knight et al.,[13] by electron spin resonance in rare gas matrices. The first calculation, identifying correctly the ground state as $X^4\Sigma^-$, was reported in 1986 by Zaitsevskii and co-workers[6] using the effective core potential approximation coupled with a limited, perturbatively selected, CI. Bauschlicher and co-workers[12] using a multireference CI methodology and a flexible enough basis set, obtained 20 states, the highest 8 being determined at the complete active space SCF (CASSCF) level. The binding energy (D_e) of the $X^4\Sigma^-$ state, $D_e = 76$ kcal/mol (Table 2), is at variance with the experimental value of 64.92 kcal/mol, measured in 1993 by fluorescence spectrometry.[16] However, it seems that the experimental value is indeed underestimated by as much as 12 kcal/mol, if compared with our results (vide infra), mainly because of the uncertainties introduced due to the use of the Birge−Sponer extrapolation method.[18] Recently, Bartlett and co-workers[14] using the CCSD-(T) approach, determined the D_e, bond length (r_e), and harmonic frequency (ω_e) of the $X^4\Sigma^-$, $a^2\Pi$, and $A^4\Pi$ states of AlC (Table 2).

Using a series of increasing size correlation consistent basis sets and a multireference CI approach, we have examined the ground state of BC molecule. In addition, 29 excited states of BC have been investigated employing a quintuple quality basis. For the AlC system, 31 states have been calculated employing a quadruple + diffuse basis set. We presently discuss the BC and AlC ground states only; the rest of the states (29 + 30) will be discussed in a forthcoming publication.[19]

With the purpose of better understanding the structure of BC and AlC we have also performed calculations on the anions BC^- and AlC^- as well as on the ground states of the linear triatomic hydrides, HBC and HAlC.

2. Basis Sets and Computational Approach

For the BC molecule the correlation consistent basis sets of Dunning and co-workers were employed.[20] In particular, for both the B and C atoms the following series of basis sets were used: cc-pV*n*Z, aug-cc-pV*n*Z, cc-pCV*n*Z, and aug-cc-pCV*n*Z, where $n = 2$(D), 3(T), 4(Q), and 5. The augmented bases (aug-), include one extra diffuse set of functions for every different

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TABLE 1: Existing Theoretical and Experimental Data on the Ground $X^4\Sigma^-$ State of the BC Molecule: Energies E (hartrees), Dissociation Energies D_e (kcal/mol), Bond Lengths r_e (Å), Harmonic Frequencies and Anharmonic Corrections ω_e, $\omega_e x_e$ (cm^{-1}), and Dipole Moments μ (D)

method	-E	D_e	r_e	ω_e	$\omega_e x_e$	μ
VCI[a]	62.282846	70.24	1.665	991	10.39	
MRCI[b]		88.6	1.53	1140	10.5	
MRD-CI[c]	62.4978	93.7	1.501	1140	8.5	1.024/0.513
MRCISD[d]	62.6090		1.521			0.725
UHF[e]	62.3425		1.429			
MCSCF (6)[e]	62.3553		1.461			
CCSD(T)[e]	62.6291		1.491			
UHF−CCSD(T)[f,g]	62.55611		1.5027	1083		
UHF−CCSD(T)[f,h]	62.53395		1.5078	1092.3	28.2	
RHF−CCSD(T)[f,h]	62.53416		1.5015	1147.9	10.2	
RHF−CCSD(T)[f,i]	62.54556					
B3LYP[j]	62.224208	71.16	1.48			
expt		106 ± 7[k]	1.49116(34)[l]	1172.6[m]	10.3[m]	

[a] Reference 5, valence CI, minimal Slater basis set; 54 states obtained 19 of which are bound. [b] Reference 6, effective core potential approximation, DZ+P valence STO basis set; four states examined, $X^4\Sigma^-$, $^2\Pi$, $^2\Delta$, $^2\Sigma^-$. [c] Reference 7, $[6s4p1d]_{B,C}$ basis set; 20 states examined, r_e, ω_e, and $\omega_e x_e$, values are given for the 12 lowest states. [d] Reference 4, $[9s7p3d]_{B,C}$ basis set; valence + core single + selected double excitations. [e] Reference 8, 50 numerical orbitals employed; all electrons included in the CCSD(T). [f] Reference 9. [g] TZ+2P basis set. [h] cc-pVTZ basis set. [i] cc-pVQZ basis set. [j] Reference 10. [k] Reference 3, mass spectrometry. [l] Reference 11, Fourier transform emission specroscopy; two states have been identified, the $X^4\Sigma^-$ and $B^4\Sigma^-$. [m] Reference 1, Fourier transform spectroscopy in solid neon; five states have been identified, the $X^4\Sigma^-$, $A^4\Pi$, $B^4\Sigma^-$, $a^2\Pi$, and $d^2\Sigma^+$.

TABLE 2: Existing Theoretical and Experimental Data on the Ground $X^4\Sigma^-$ State of the AlC Molecule: Energies E (hartrees), Dissociation Energies D_e (kcal/mol), Bond Lengths r_e (Å), Harmonic Frequencies and Anharmonic Corrections ω_e, $\omega_e x_e$ (cm^{-1}), and Dipole Moments μ (D)

method	-E	D_e	r_e	ω_e	$\omega_e x_e$	μ
MRCI[a]		79.5	1.92	629	6.2	
SA-MRCI[b]		76	1.978	629		
MP2[c]	279.6577		1.799			3.35
CI[c]	279.7700		1.980			2.5
CCSD(T)[d]	280.014465	78.6	1.9544	658		
expt[e]			1.95503	654.84	4.293	
expt[f]		64.920		639.3	4.5	
expt[g]				640.1[g,h]		
				629.8[g,i]		

[a] Reference 6, effective core potential approximation, DZ+P valence STO basis set; four states examined, $X^4\Sigma^-$, $^2\Pi$, $^2\Delta$, $^2\Sigma^-$. [b] Reference 12, state average MRCI, [5s4p2d1f/4s3p2d1f] basis set; 19 states examined, 12 of which were examined at the MRCI level of theory, the rest at the CASSCF. [c] Reference 13, 6-31G* basis set. [d] Reference 14, [7s7p5d4f/7s7p4d3f] basis set, all electrons correlated; three states examined, $X^4\Sigma^-$, $^2\Pi$, and $^4\Pi$. [e] Reference 15, emission spectroscopy; two states have been identified, the $X^4\Sigma^-$ and $B^4\Sigma^-$ state. [f] Reference 16, fluorescence spectroscopy in solid argon; two states identified, the same as in e. [g] Reference 17, infrared spectroscopy. [h] Grain surface value. [i] Argon matrix value.

angular momentum of the plain (nonaugmented) basis. The core (C) bases, include {(n − 1)s, (n − 1)p, (n − 2)d, (n − 3)f...} "tight" Gaussians grafted to the corresponding plain set, where n is the cardinality of the basis set. Our largest aug-cc-pCV5Z basis $(19s13p8d6f4g2h)_{B,C}$ generally contracted to $[11s10p8d6f4g2h]_{B,C}$, contains 362 spherical Gaussian functions, as compared to 290 and 254 contracted functions of the cc-pCV5Z and aug-cc-pV5Z, respectively.

For the AlC system a single basis set was employed, namely the aug-cc-pVQZ, [7s6p4d3f2g/Al 6s5d4d3f2g/$_C$] numbering 164 contracted functions. The same basis, i.e., the aug-cc-pVQZ, was used for the anions BC^- and AlC^-. For the hydrogenated species HBC and HAlC, the basis set used are $(\text{cc-pVQZ})_H$/(cc-pV5Z without the h functions)$_{B,C}$, and $(\text{cc-pVQZ})_H$/(aug-cc-pVQZ)$_{Al,C}$, respectively.

The complete active space self-consistent field plus single plus double replacements (CASSCF + 1 + 2 = MRCI) approach was followed, implemented at the CI level by the internal contraction (ic) scheme.[21] The reference space was defined by distributing 7 (BC, AlC) or 8 (BC^-, AlC^-, HBC, HAlC) "valence" (active) electrons to 8 (one 2s + three 2p on B + one 2s + three 2p on C), or 9 (+ one 1s on H) orbital functions. Depending on the number of orbitals and the symmetry of the state, the reference spaces range from 352 configuration functions ($^4\Sigma^-$, BC and AlC), to 1880 CFs ($^3\Sigma^-$, HBC and HAlC). The CI spaces, in the BC $^4\Sigma^-$ state for instance, range from 90 832 (cc-pVDZ) to 322 035 200 (aug-cc-pCV5Z) uncontracted CFs; the corresponding internally contracted numbers are ∼12 000, and 4 000 000 CFs, respectively. Although the internal contraction scheme reduces the dynamical space dramatically, the corresponding energy losses are far from being analogous.[22] For example, at the MRCI/cc-pVDZ level, the energy loss due to the internal contraction in the BC molecule ($X^4\Sigma^-$) is 1.4 mhartrees.

The spectroscopic constants (r_e, ω_e, $\omega_e x_e$, α_e, and $\bar{D}_e$) were obtained by a Dunham analysis, after always fitting 12 points of the potential energy curve (CASSCF, MRCI) to a seventh degree polynomial, and up to an intermolecular distance $r - r_e$ = 0.7 bohr.

For the calculations the MOLPRO96 and MOLPRO2000 packages were used.[23] Some of our results have also been checked by the COLUMBUS code.[24]

3. Results and Discussion

In what follows we discuss the ground states of BC and AlC molecules, the ground and two more excited states of the anions BC^- and AlC^- ($X^3\Pi$, $A^3\Sigma^-$, $a^1\Sigma^+$), and the ground $^3\Sigma^-$ (linear) electronic structures of the triatomics H−BC and H−AlC. For the ground $X^4\Sigma^-$ states of BC and AlC we report absolute energies, dissociation energies (D_e), bond distances (r_e), dipole moments (μ), Mulliken charges (q), harmonic frequencies and anharmonic corrections (ω_e, $\omega_e x_e$), rotational vibrational couplings (α_e), and centrifugal distortions ($\bar{D}_e$). Full potential energy curves (PEC) are also reported for both molecules, BC and AlC. Practically, the same information is also given for the anions and the triatomics HBC and HAlC.

3.1. BC. The ground state of the BC molecule is of $^4\Sigma^-$ symmetry, with its first excited $^2\Pi$ state 10.5 kcal/mol higher.[19] The $X^4\Sigma^-$ state correlates to the ground state atoms, B(^{2}P;M=0) + C(^{3}P;M=0). The leading CASSCF equilibrium configuration

TABLE 3: Absolute Energies E (hartrees), Dissociation Energies D_e (kcal/mol), Bond Distances r_e (Å), Dipole Moments μ (D), Mulliken Charges on the C Atom q_c, Harmonic Frequencies ω_e (cm^{-1}), First Anharmonic Corrections $\omega_e x_e$ (cm^{-1}), Rotational Vibrational Couplings α_e (cm^{-1}), and Centrifugal Distortions $\bar{D}_e$(cm^{-1}), of the Ground $X^4\Sigma^-$ State of the $^{11}B^{12}C$ Molecule, in CASSCF, MRCI, MRCI+Q[a]/ (aug)-cc-p(C)VnZ, n = 2, 3, 4, and 5 Methods

method	$-E$	D_e	r_e	μ	q_c	ω_e	$\omega_e x_e$	$10^{-2}\alpha_e$	$10^{-6}\bar{D}_e$
expt		106 ± 7[b]	1.49116(34)[c]			1172.6[d]	10.3[d]		
cc-pVDZ									
CASSCF	62.405644	90.47	1.5228	0.673	−0.06	1132.2	9.72	1.59	6.33
MRCI	62.495983	92.85	1.5286	0.649	−0.06	1121.3	9.45	1.56	6.31
MRCI+Q	62.5003	92.8	1.532						
cc-pVTZ									
CASSCF	62.414869	91.90	1.5124	0.743	−0.03	1132.7	10.39	1.60	6.59
MRCI	62.531848	98.44	1.5063	0.846	−0.03	1148.3	10.19	1.58	6.57
MRCI+Q	62.5382	98.5	1.508						
cc-pVQZ									
CASSCF	62.418147	92.20	1.5094	0.775	−0.13	1134.0	9.44	1.60	6.66
MRCI	62.542941	100.39	1.4992	0.925	−0.13	1159.1	10.11	1.64	6.64
MRCI+Q	62.5499	100.6	1.500						
cc-pV5Z									
CASSCF	62.418721	92.20	1.5091	0.779	−0.16	1134.6	9.80	1.62	6.66
MRCI	62.546026	100.93	1.4977	0.947	−0.15	1161.8	10.56	1.67	6.65
MRCI+Q	62.5531	101.1	1.499						
CBS limit									
MRCI	62.5476 ± 2	101.3±.1	1.4967 ± 5	0.965 ± 7		1164 ± 1			
aug-cc-pVDZ									
CASSCF	62.407334	90.87	1.5202	0.800	−0.06	1119.0	8.31	1.86	6.55
MRCI	62.502161	93.41	1.5272	0.825	−0.08	1115.2	10.05	1.63	6.42
MRCI+Q	62.5073	93.2	1.531						
aug-cc-pVTZ									
CASSCF	62.415194	91.99	1.5115	0.770	−0.02	1131.1	9.69	1.61	6.64
MRCI	62.533880	98.98	1.5054	0.899	−0.04	1145.9	10.04	1.64	6.63
MRCI+Q	62.5406	99.1	1.507						
aug-cc-pVQZ									
CASSCF	62.418201	92.17	1.5091	0.777	−0.18	1134.4	10.98	1.79	6.60
MRCI	62.543651	100.60	1.4993	0.938	−0.20	1158.3	9.95	1.62	6.64
MRCI+Q	62.5506	100.8	1.501						
aug-cc-pV5Z									
CASSCF	62.418739	92.22	1.5091	0.779	−0.22	1134.6	9.79	1.62	6.66
MRCI	62.546320	101.03	1.4978	0.950	−0.24	1161.3	10.15	1.64	6.65
MRCI+Q	62.5534	101.2	1.499						
aug-CBS limit									
MRCI	62.5477 ± 2	101.2	1.4971 ± 1	0.965 ± 7		1164 ± 1			
$1s^2$ electrons included in MRCI									
cc-pCVDZ									
CASSCF	62.406018	90.60	1.5212	0.688	−0.07	1131.5	9.74	1.58	6.38
MRCI	62.566948	93.61	1.5250	0.696	−0.07	1125.8	9.59	1.56	6.35
MRCI+Q	62.5744	93.5	1.529						
cc-pCVTZ									
CASSCF	62.415241	92.02	1.5109	0.757	−0.10	1131.8	9.68	1.62	6.64
MRCI	62.623400	99.45	1.5002	0.875	−0.11	1158.0	9.59	1.56	6.35
MRCI+Q	62.6340	99.4	1.502						
cc-pCVQZ									
CASSCF	62.418222	92.20	1.5092	0.776	−0.11	1134.6	9.77	1.62	6.66
MRCI	62.641146	101.42	1.4933	0.925	−0.10	1170.7	10.13	1.64	6.66
MRCI+Q	62.6526	101.5	1.495						
cc-pCV5Z									
CASSCF	62.418782	92.24	1.5090	0.779	−0.13	1134.6	9.79	1.62	6.60
MRCI	62.646171	102.00	1.4918	0.944	−0.12	1173.7	10.27	1.63	6.67
MRCI+Q	62.6577	102.1	1.493						
core-CBS limit									
MRCI	62.6487 ± 3	102.3± .1	1.4910 ± 2	0.949 ± 3		1176 ± 1			
aug-cc-pCVDZ									
CASSCF	62.407747	91.04	1.5193	0.796	−0.09	1130.7	9.85	1.60	6.44
MRCI	62.573209	94.48	1.5227	0.856	−0.10	1122.0	9.96	1.61	6.45
MRCI+Q	62.5816	94.1	1.527						
aug-cc-pCVTZ									
CASSCF	62.415538	92.10	1.5107	0.776	−0.15	1132.4	9.74	1.61	6.64
MRCI	62.625190	99.92	1.5001	0.910	−0.17	1157.2	10.00	1.62	6.64
MRCI+Q	62.6361	99.9	1.502						

TABLE 3 (Continued)

method	-E	D_e	r_e	μ	q_c	ω_e	$\omega_e x_e$	$10^{-2}\alpha_e$	$10^{-6}\bar{D}_e$
				aug-cc-pCVQZ					
CASSCF	62.418288	92.22	1.5098	0.778	−0.12	1134.5	9.79	1.62	6.66
MRCI	62.641790	101.62	1.4934	0.934	−0.13	1170.2	10.08	1.63	6.66
MRCI+Q	62.6533	101.7	1.497						
				aug-cc-pCV5Z					
CASSCF	62.418759	92.22	1.5097	0.782	−0.17	1134.1	9.32	1.63	6.67
MRCI	62.646425	102.06	1.4919	0.939	−0.19	1173.5	10.12	1.64	6.67
MRCI+Q	62.658021	102.2	1.493						
				core-aug-CBS limit					
MRCI	62.6489 ± 4	102.3± .1	1.4911 ± 3	0.945 ± 4		1176 ± 1			

[a] Multireference Davidson correction, ref 26. [b] Reference 3, D_o value. [c] Reference 11. [d] Reference 1.

and the Mulliken populations (at the cc-pV5Z basis) are (B/C)

$$|X^4\Sigma^-\rangle \sim 0.97|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1\, 1\pi_y^1\rangle$$

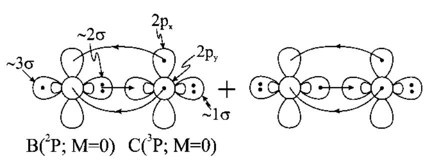
$$2s^{1.36}2p_z^{0.67}\ 2p_x^{0.37}\ 2p_y^{0.37}/2s^{1.69}2p_z^{1.16}\ 2p_x^{0.63}\ 2p_y^{0.63}$$

(Notice that the numbering of molecular orbitals above refers to "active" orbitals only.)

Taking into account the asymptotic populations

$$2s^{1.89}2p_z^{1.00}\ 2p_x^{0.05}\ 2p_y^{0.05}/2s^{1.95}2p_z^{0.05}\ 2p_x^{1.00}\ 2p_y^{1.00}$$

upon the bond formation 2 × 0.32 e$^-$ are transferred from C to B via the π frame giving rise to two half π bonds. Along the σ route 0.85 e$^-$are migrating from the $(sp_z)^{2.89}$ B hosted functions to the C $2p_z$ orbital. Although the bonding along the σ frame is rather unclear, we think that the following superposition of valence-bond-Lewis (vbL) icons captures the essence of it.



These drawings suggest that the two atoms are held together by two half π bonds, and an "incomplete" σ bond. The following CAS orbitals support the above superposition concerning the σ-interaction,

$$1\sigma = (0.79)2s(C) + (0.30)2p_z(C) + (0.56)2s(B) + (-0.38)2p_z(B)$$

$$2\sigma = (-0.56)2s(C) + (0.57)2p_z(C) + (0.65)2s(B)$$

$$3\sigma = (0.56)2p_z(C) + (0.47)2s(B) + (-0.78)2p_z(B)$$

We can claim that the 1σ orbital is practically a $2s2p_z$ hybrid on carbon, while the 2σ and 3σ represent the harpoon-like 2e$^-$ (left icon), and 1e$^-$ (right icon) σ interactions, respectively.

Table 3 lists all our numerical findings in a series of increasing size correlation consistent basis sets, double through quintuple, and complete basis set (CBS) MRCI limits for the total energy, D_e, r_e, μ and ω_e parameters. The CBS limits have been obtained by applying the simple exponential function of the form[25]

$$P_n = P_{CBS} + a e^{-bn}$$

where a and b are adjustable parameters, and n = 2, 3, 4 and 5 is the cardinal basis set number.

From Table 3 it is clear that the simple exponential formula works well in the present case, although all CBS limits are only slight improvements over the results of the corresponding higher angular momentum set. We observe that the diffuse functions (aug- bases) do not play any significant role in all calculated properties of the BC system. Also, the inclusion of the core functions is not very important, at least for this system, with the largest effect being the decrease of the B−C bond length by 0.006 Å at the MRCI/cc-pCV5Z level as contrasted to the plain set, a rather well-known result by now.[27−29] At the highest level of calculation, namely, MRCI/aug-cc-pCVnZ-CBS we obtain r_e = 1.4911 ± 0.0003 Å, in excellent agreement with the experimental value[11] of 1.491 16 ± 0.000 34 Å. At the same level our D_e value is 102.3 ± 0.1 kcal/mol (identical to the MRCI/cc-pVnZ-CBS). Scalar relativistic corrections (mass velocity + Darwin terms) + spin−orbit corrections obtained from experimental atomic values[30] (assuming zero first-order spin−orbit splitting of the $X^4\Sigma^-$ state, see ref 31), amount to a 0.15 kcal/mol reduction of the calculated D_e value. Thus, our best D_e value of 102.2 ± 0.1 kcal/mol is more accurate than the experimental value[3] of $D_e = D_0 + \omega_e/2$ = 106 ± 7 kcal/mol + 1172.6/2 cm^{-1} = 108 ± 7 kcal/mol. Notice also that the best calculated ω_e and $\omega_e x_e$ values of ^{11}B−C are in agreement with the experiment (Table 3). The corresponding ω_e and $\omega_e x_e$ values for the ^{10}B−C species are 1203.7 and 10.8 cm^{-1}, respectively.

Now, our calculated dipole moments converge almost to the same CBS value for all four kinds of basis sets used in the present study (Table 3). Our (formally) best value at the MRCI/aug-cc-pCVnZ-CBS level is 0.945 ± 0.004 D as contrasted to previous calculated values, 0.513 or 1.024 D (depending on the orbitals used),[7] and 0.725 D.[4]

Finally, Figure 1 shows potential energy curves at the MRCI/aug-cc-pVnZ, n = 2, 3, 4 and 5 level of theory.

3.2. AlC. The ground state of AlC is of $^4\Sigma^-$ symmetry, tracing its lineage to the ground-state atoms Al(^{2}P;M=0) + C(^{3}P;M=0). The dominant CASSCF equilibrium configuration (active orbitals only) and Mulliken equilibrium and asymptotic atomic distributions (Al/C) are

$$|X^4\Sigma^-\rangle \sim 0.96|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1\, 1\pi_y^1\rangle$$

$$3s^{1.72}3p_z^{0.47}\ 3p_x^{0.14}\ 3p_y^{0.14}/2s^{1.74}2p_z^{0.90}\ 2p_x^{0.89}2p_y^{0.89}$$

$$3s^{1.91}3p_z^{1.01}\ 3p_x^{0.04}\ 3p_y^{0.04}/2s^{1.95}2p_z^{0.05}\ 2p_x^{1.00}\ 2p_y^{1.00}$$

As in the BC system we can easily discern the formation, albeit weaker, of two half π bonds caused by the transfer of 2 × 0.11

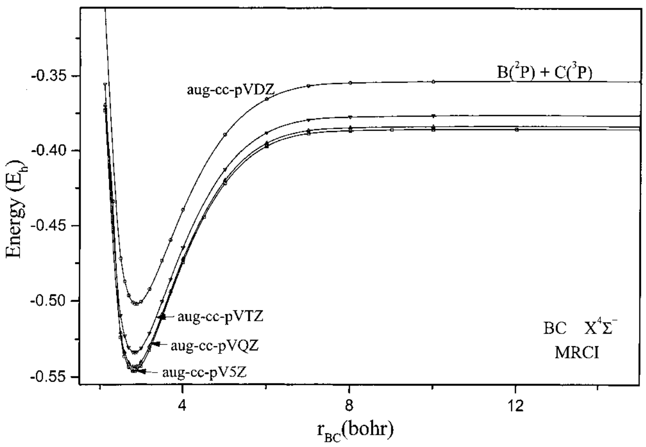


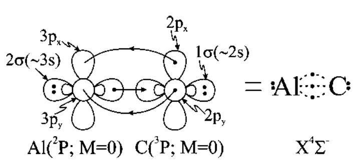
Figure 1. Potential energy curves of the BC $X^4\Sigma^-$ state at the MRCI/aug-cc-pV*n*Z, $n = 2$, 3, 4, and 5 level of theory. All energies are shifted by +62 E_h.

e^- through the π system from C to Al. Along the σ frame $0.90 - 0.26 = 0.64$ e^- are transferred to the C(2p_z) orbital from the Al$(3s3p_z)^{2.92}$ asymptotic distribution, giving rise to a half σ bond, as is also evinced from the 2σ and 3σ orbital expressions:

$$2\sigma = (0.90)3s(Al) + (0.29)3p_z(Al) + (-0.33)2s(C) + (0.12)2p_z(C)$$

$$3\sigma = (0.58)3p_z(Al) + (0.30)2s(C) + (-0.83)2p_z(C)$$

So, the nature of σ bonding differs from the corresponding σ interaction of the isovalent BC, represented by the following vbL icon implying three half bonds. Overall, 0.44 e^- is migrating



from Al to C as compared to 0.18 e^- in the BC system at the same level of theory.

Now Tables 4 and 5 collect the calculated properties of the AlC $X^4\Sigma^-$ state along with calculated properties of the anions BC^- and AlC^- (vide infra). The discrepancy between the experimental[16] and calculated D_e values of 12.6 kcal/mol or 20% is the first thing that catches the eye. The quality of our calculations is such that we feel confident to claim that the experimental number[16] is in error. Scalar relativistic and spin−orbit corrections (vide supra) amount to a decrease of D_e by 0.10 + 0.26 kcal/mol, respectively. Therefore, our D_e MRCI/aug-cc-pVQZ value is 77.13 kcal/mol. Assuming that in going from the aug-cc-pVQZ to the CBS limit the increase in binding will be equal to the corresponding increase in the BC molecule, i.e., 1.8 kcal/mol, a D_e value of 80 kcal/mol seems more realistic.

The agreement between experiment[15] and theory of the bond distance can be considered as acceptable but not quite good, assuming of course that the experimental number is correct. However, there is no doubt that the increase of the basis set will decrease the r_e value, and hypothesizing a decrease of 0.008 Å in going from the aug-cc-pVQZ to the core CBS limit as in the isovalent BC molecule, our r_e value becomes 1.963 Å, now in reasonable agreement with the experiment. Finally, the MRCI value of the dipole moment, $\mu = 1.619$ D, is at variance with previously calculated values, $\mu = 3.35$ and 2.5 D (Table 2). Figure 2 gives the MRCI potential energy curve of AlC.

TABLE 4: Absolute Energies *E* (hartrees), Dissociation Energies with Respect to Their Asymptotic Products D_e (kcal/mol), Bond Lengths r_e (Å), Electron Affinities EA (eV), Separation Energies T_e (kcal/mol), and Asymptotic Products, of AlC ($X^4\Sigma^-$), AlC^- ($X^3\Pi$, $A^3\Sigma^-$, $a^1\Sigma^+$), and BC^- ($X^3\Pi$, $a^1\Sigma^+$, $A^3\Sigma^-$) Molecules, at the CASSCF, MRCI and MRCI+Q/aug-cc-pVQZ Level. Experimental and Existing Theoretical Data are also Included

method	-*E*	D_e	r_e	EA	T_e
		AlC			
		$AlC(X^4\Sigma^-) \to C(^3P;M = 0) + Al(^2P; M = 0)$			
CASSCF	279.717306	68.25	1.9797		
MRCI	279.838353	77.49	1.9710		
MRCI+Q	279.8465	77.9	1.973		
CBS-estimated		80			
expt		64.92[a]	1.95503[b]		
		AlC^-			
		$AlC^-(X^3\Pi) \to C^-(^4S) + Al(^2P; M = \pm1)$			
CASSCF	279.721638	75.34	1.9087	0.118	0.0
MRCI	279.874505	77.16	1.8945	0.984	0.0
MRCI+Q	279.8891	76.5	1.895	1.2	0.0
CCSD(T)[c]	280.054044	77.3	1.8708	1.077	0.0
		$AlC^-(A^3\Sigma^-) \to C^-(^4S) + Al(^2P; M = 0)$			
CASSCF	279.707965	65.41	1.9785	−0.254	8.58
MRCI	279.864848	71.77	1.9558	0.721	6.06
MRCI+Q	279.8802	71.1	1.957	0.92	5.6
ROHF[d]	279.623	42.7	1.8464	−1.65[d]	
CCSD(T)[c]	280.046892		1.9363	0.882	4.49
		$AlC^-(a^1\Sigma^+) \to C(^3P; M = 0) + Al^-(^3P; M = 0)$			
CASSCF	279.714740	73.28	1.8203	−0.070	4.33
MRCI	279.857980	83.14	1.8117	0.534	10.4
MRCI+Q	279.8698	82.8	1.815	0.63	12
CCSD(T)[c]	280.036378		1.7961	0.596	11.09
		BC^-			
		$BC^-(X^3\Pi) \to C^-(^4S) + B(^2P; M = \pm1)$			
CASSCF	62.445889	110.01	1.4593	0.753	0.0
MRCI	62.610381	118.67	1.4445	2.45	0.0
MRCI+Q	62.6236	118.8	1.444	2.0	0.0
?[e]			1.39		
		$BC^-(a^1\Sigma^+) \to C(^3P; M = 0) + B^-(^3P; M = 0)$			
CASSCF	62.455482	133.03	1.3964	1.01	−6.02
MRCI	62.607863	139.66	1.3845	1.75	1.58
MRCI+Q	62.6183	138.1	1.385	1.8	3.3
RHF/3-21G[f]			1.3904	2.29[f]	
MP2(full)[g]		142.5	1.391	2.850[g]	
MP4//MP2[g]		134.1		3.100[g]	
MP2(full)[h]			1.383	3.102[h]	
MP4//MP2[h]				3.329[h]	
?[e]			1.32		
		$BC^-(A^3\Sigma^-) \to C^-(^4S) + B(^2P; M = 0)$			
CASSCF	62.429311	98.88	1.5103	0.302	10.4
MRCI	62.596103	110.11	1.4977	1.43	8.96
MRCI+Q	62.6100	110.9	1.498	1.6	8.6
?[e]			1.45		
expt[i]				2.8 ± 0.3	

[a] Reference 16. [b] Reference 15. [c] Reference 14, [7s7p5d4f/7s7p4d3f] basis set; all electrons have been correlated. The spin contamination is 3.157 ($X^3\Pi$) and 3.003 ($A^3\Sigma^-$). [d] Reference 35, 6-311G* basis set, vertical detachment energy. [e] Reference 32, estimated value from data for isoelectronic species. [f] Reference 33, vertical detachment energy. [g] Reference 33, 6-31+G(d) basis set, vertical detachment energy. [h] Reference 34, 6-311+G(df) basis set, vertical detachment energy. [i] Reference 32, estimated electron affinity by charge inversion spectrometry.

3.3. Anions BC^- and AlC^-. It is interesting that there is no consensus in the literature as for the ground state of the anion BC^- or the electron affinity (EA) of BC; experimentally, there is an estimated EA of +2.8 ± 0.3 eV.[32] Theoretically, we are aware of two articles both reporting on the $^1\Sigma^+$ state of BC^-

TABLE 5: Mulliken Charges on the C Atom q_c, Harmonic Frequencies ω_e (cm^{-1}), First Anharmonic Corrections $\omega_e x_e$ (cm^{-1}), Rotational Vibrational Couplings α_e (cm^{-1}) and Centrifugal Distortions $\bar{D}_e$(cm^{-1}), of the AlC ($X^4\Sigma^-$), AlC$^-$ ($X^3\Pi$, $A^3\Sigma^-$, $a^1\Sigma^+$), and BC$^-$ ($X^3\Pi$, $a^1\Sigma^+$, $A^3\Sigma^-$) Molecules, at the CASSCF, MRCI/aug-cc-pVQZ Level. Experimental and Existing Theoretical Data are also Included

method	q_c	ω_e	$\omega_e x_e$	α_e (10^{-2})	$\bar{D}_e$ (10^{-6})
		AlC($X^4\Sigma^-$)			
CASSCF	−0.44	645.8	6.33	0.66	1.33
MRCI	−0.48	654.2	6.76	0.45	1.33
expt[a]		654.84	4.293		
expt[b]		639.3	4.5		
expt[c]		640.0			
		AlC$^-$($X^3\Pi$)			
CASSCF	−0.81	709.0	10.1	0.76	1.35
MRCI	−0.85	718.8	5.35	0.56	1.40
CCSD(T)[d]		747			
		AlC$^-$($A^3\Sigma^-$)			
CASSCF	−0.72	659.5	4.60	0.51	1.28
MRCI	−0.75	681.7	4.72	0.50	1.29
CCSD(T)[d]		701			
		AlC$^-$($a^1\Sigma^+$)			
CASSCF	−0.85	805.8	5.10	0.55	1.42
MRCI	−0.88	810.1	5.59	0.57	1.44
CCSD(T)[d]		835			
		BC$^-$($X^3\Pi$)			
CASSCF	−0.60	1267.0	9.16	1.56	6.53
MRCI	−0.59	1301.4	9.82	1.55	6.59
		BC$^-$($a^1\Sigma^+$)			
CASSCF	−0.58	1421.8	9.93	1.50	6.75
MRCI	−0.59	1440.9	10.2	1.56	6.92
MP2(full)[e]		1587.7			
MP2(full)[f]		1592.5			
		BC$^-$($A^3\Sigma^-$)			
CASSCF	−0.41	1171.3	9.10	1.48	6.22
MRCI	−0.40	1198.2	9.33	1.49	6.25

[a] Reference 15. [b] Reference 16. [c] Reference 17. [d] Reference 14. [e] Reference 34, 6-31+G(d) basis set. [f] Reference 34, 6-311+G(df) basis set.

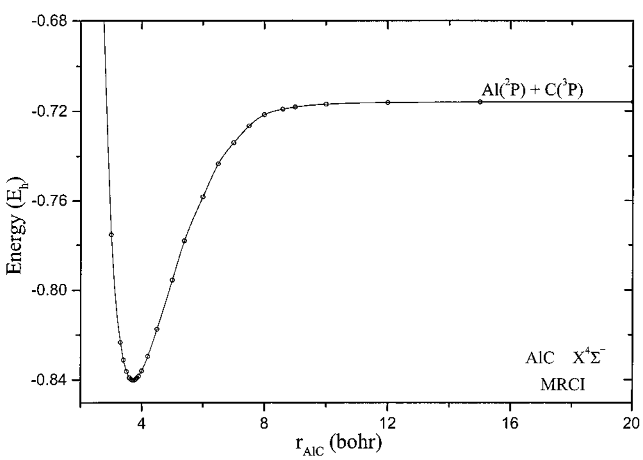


Figure 2. Potential energy curve of the AlC $X^4\Sigma^-$ state at the MRCI/aug-cc-pVQZ level. All energies are shifted by +279 E_h.

(which, as it turns out, is the first excited state (vide infra)), at the RHF/3-21G,[33] and MP4/6-311+G(d,f)//MP2/6-311+G(d,f)[34] level of theory.

Concerning the AlC$^-$ anion and as far as we know, there is no experimental information in the literature. Theoretically, a ROHF/6-311G* level investigation[35] reports on the $^3\Sigma^-$ state (which was proved to be the first excited state of AlC), giving a (vertical) EA of −1.65 eV (BC$^-$ unbound with respect to BC), and a very recent article by Gutsev et al.,[14] at the CCSD(T)/[7s7p5d4f/7s7p4d3f] level; these workers examined the $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$ states (Tables 4 and 5).

With the purpose of clarifying the matter on the BC$^-$ system, to extend and/or improve the information on AlC$^-$, and to, perhaps, gain some insights on the bonding of the neutral species in conjunction with the anion's bonding, we have performed MRCI/aug-cc-pVQZ calculations. For both anions and for the states $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$ we report absolute energies, PECs, D_e's, r_e's, EAs, q's, ω_e's, $\omega_e x_e$'s, α_e's, and $\bar{D}_e$'s.

3.3a. $X^3\Pi$ States. We define the electron affinity (EA) of a species X (atom or molecule) by the process X + e$^-$ → X$^-$ + EA, with X and X$^-$ in their ground electronic states; EA is positive assuming X$^-$ to be bound with respect to X. Table 6 lists absolute energies of the ground states of B, C, and Al atoms, their anions and calculated and experimental EAs.[36]

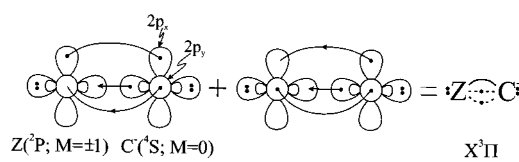
Both BC$^-$ and AlC$^-$ correlate to their ground-state fragments, i.e., B, Al(^{2}P;M=±1) + C$^-$(^{4}S). The leading equilibrium CASSCF CFs and Mulliken populations (B, Al/C) are

$$\mathrm{BC^-, AlC^-:}\quad |X^3\Pi\rangle \sim 1/\sqrt{2} \times 0.93|1\sigma^2 2\sigma^2 3\sigma^1(1\pi_x^1\,1\pi_y^2 + 1\pi_x^2\,1\pi_y^1)\rangle$$

$$\mathrm{BC^-:}\quad 2s^{1.45}2p_z^{0.67}\,2p_x^{0.62}\,2p_y^{0.62}/2s^{1.73}2p_z^{1.09}\,2p_x^{0.87}2p_y^{0.87}$$

$$\mathrm{AlC^-:}\quad 3s^{1.67}3p_z^{0.56}\,3p_x^{0.46}\,3p_y^{0.46}/2s^{1.78}2p_z^{0.92}\,2p_x^{1.04}\,2p_y^{1.04}$$

A comparison of BC$^-$ and AlC$^-$ $X^3\Pi$ states with the corresponding ground-state neutrals is inappropriate, because in the former the in situ B and Al atoms find themselves in a $|^2P; M = \pm1\rangle$ state as opposed to the $|^2P; M = 0\rangle$ in the neutrals. The electronic configurations and populations dictate the following vbL picture for both anions (Z = B, Al),suggesting



that the bonding is composed of $^3/_2$ π and $^1/_2$ σ bonds. Overall, about 0.4 and 0.2 e$^-$ are transferred from C$^-$ to the B or Al atoms, respectively. Observe (Table 4) that the $X^3\Pi$ state of the AlC$^-$ has a D_e = 77.16 kcal/mol, practically equal to the D_e of the neutral, while the D_e of BC$^-$ ($X^3\Pi$) is by 18 kcal/mol higher than the BC species at the same level of theory (MRCI/aug-cc-pVQZ). It is also interesting to note that the bond lengths of the BC$^-$ and AlC$^-$ anions are significantly shorter as compared to the neutrals, 0.055 and 0.076 Å, respectively at the MRCI/ aug-cc-pVQZ level of theory (Tables, 3 and 4). Figures 3 and 4 present the $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$ PECs of the BC$^-$ and AlC$^-$.

3.3b $a^1\Sigma^+$ States. From Table 4 we read that the first excited state of BC$^-$ is of $^1\Sigma^+$ symmetry, while for AlC$^-$ $^1\Sigma^+$ is the symmetry of the second excited state, 1.58 and 10.4 kcal/mol above the $X^3\Pi$ states, respectively. The dominant CASSCF CF for both species and Mullliken populations are (B$^-$, Al$^-$/C)

$$\mathrm{BC^-, AlC^-:}\quad |a^1\Sigma^+\rangle \sim 0.86|1\sigma^2 2\sigma^2 1\pi_x^2\,1\pi_y^2\rangle$$

$$\mathrm{BC^-:}\quad 2s^{1.22}2p_z^{0.52}\,2p_x^{0.83}\,2p_y^{0.83}/2s^{1.50}2p_z^{0.75}\,2p_x^{1.15}2p_y^{1.15}$$

$$\mathrm{AlC^-:}\quad 3s^{1.32}3p_z^{0.36}\,3p_x^{0.75}\,3p_y^{0.75}/2s^{1.68}2p_z^{0.63}\,2p_x^{1.25}\,2p_y^{1.25}$$

TABLE 6: Ground Absolute Energies of C, B, and Al Atoms, their Anions, and Electron Affinities EA (eV) at the CASSCF, MRCI and MRCI+Q Level

	B/B$^-$			C/C$^-$			Al/Al$^-$		
method	B(^{2}P)	B$^-$(^{3}P)	EA	C(^{3}P)	C$^-$(^{4}S)	EA	Al(^{2}P)	Al$^-$(^{3}P)	EA
CAS	−24.560 169	−24.529 153	−0.844	−37.705 611	−37.708 496	0.079	−241.894 547	−241.883 397	−0.303
MRCI	−24.601 172	−24.605 973	0.131	−37.785 224	−37.824 674	1.073	−241.933 717	−241.946 205	0.340
MRCI+Q	−24.6025	−24.6120	0.26	−37.7883	−37.8323	1.20	−241.9357	−241.9515	0.43
expt[a]			0.277(10)			1.2629(3)			0.441(10)

[a] Reference 36.

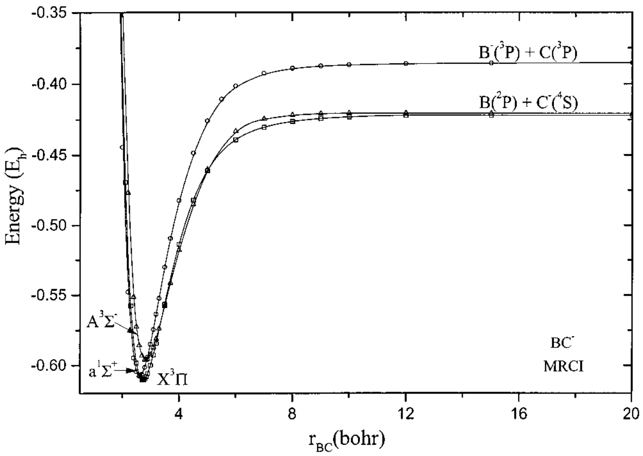


Figure 3. $X^3\Pi$, $a^1\Sigma^+$, and $A^3\Sigma^-$ potential energy curves of the BC$^-$ species at the MRCI/aug-cc-pVQZ level of theory.

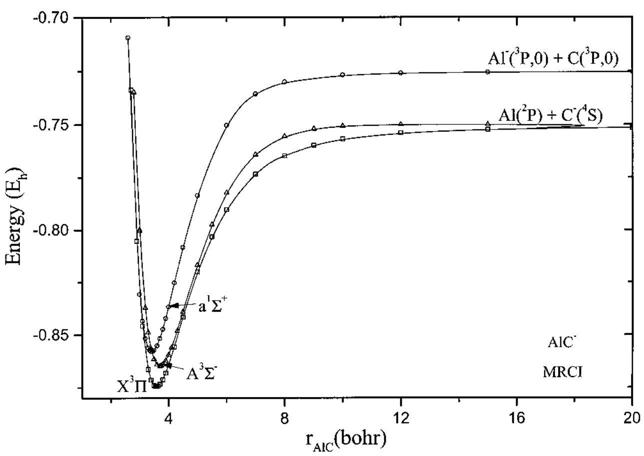
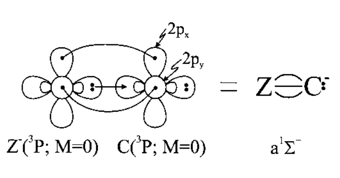


Figure 4. $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$ potential energy curves of the AlC$^-$ species at the MRCI/aug-cc-pVQZ level of theory.

The bonding in both systems can be pictorially represented by the diagram (Z = B, Al), suggesting a genuine triple bond,



two π ([0.83 + 1.15] × 2e$^-$ in the BC$^-$ or [0.75 + 1.25] × 2e$^-$ in the AlC$^-$ system), and one σ bond. Along the π frame 0.34 and 0.50 e$^-$, and along the σ frame 0.25 and 0.32 e$^-$, are transferred from B$^-$ and Al$^-$ to the C atom.

The bonding is similar to that of the $C_2(X^1\Sigma_g^+)$ system,[37] isovalent and isoelectric to BC$^-$ and isovalent to AlC$^-$. For the $C_2(X^1\Sigma_g^+)$ molecule at the MRCI/cc-pV*n*Z, n = 2−5 CBS limit, Peterson[37] obtains a D_e = 145.9 kcal/mol (D_e(expt) = 147.8 ± 0.5 kcal/mol[38]), comparable to our BC$^-$ ($a^1\Sigma^+$) D_e value of 139.66 kcal/mol at the MRCI/aug-cc-pVQZ level (Table 4).

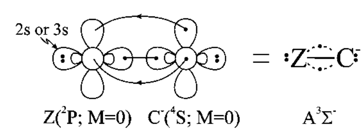
Now the $a^1\Sigma^+$ BC$^-$ and AlC$^-$ systems can be contrasted to the ground $X^4\Sigma^-$ neutral species BC and AlC; the asymptotic fragments of both pairs B$^-$ + C, Al$^-$ + C and B + C, Al + C are characterized by the same atomic quantum number $M = 0$. We note that going from BC($X^4\Sigma^-$) to BC$^-$($a^1\Sigma^+$) the D_e is increased by 39 kcal/mol (39%), as compared to 5.7 kcal/mol (7.3%) from AlC($X^4\Sigma^-$) to AlC$^-$($a^1\Sigma^+$). Clearly, the bond strengthening of the anions, as compared to the neutrals, results from the formation of an extra π bond, reflected to the shortening of the internuclear distances by 0.11 and 0.16 Å in BC$^-$ and AlC$^-$, respectively (Tables 3 and 4).

3.3c. $A^3\Sigma^-$ States. For the BC$^-$ system the $A^3\Sigma^-$ describes its second excited state, 9 kcal/mol above the X state, while it is the first excited state for the AlC$^-$ molecule, 6.1 kcal/mol higher than the ground state (Table 4). The PECs of Figures 3 and 4 indicate that the asymptotic products are C$^-$(^{4}S) + Z(^{2}P;M=0), Z = B or Al. At the equilibrium the dominant CASSCF configuration for both systems is $|A^3\Sigma^-\rangle \sim 0.97|1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^1\, 1\pi_y^1\rangle$ with the following Mulliken populations (B, Al/C$^-$)

$$\mathrm{BC^-:}\quad 2s^{1.98}2p_z^{0.93}\,2p_x^{0.31}\,2p_y^{0.31}/2s^{1.71}2p_z^{1.29}\,2p_x^{0.69}2p_y^{0.69}$$

$$\mathrm{AlC^-:}\quad 3s^{1.98}3p_z^{0.66}\,3p_x^{0.26}\,3p_y^{0.26}/2s^{1.83}2p_z^{1.41}\,2p_x^{0.72}\,2p_y^{0.72}$$

From the above it is obvious that the BC$^-$ and AlC$^-$ are held together by two half π and one σ bond; pictorially, it can be shown as



Via the π frame 2 × 0.31 and 2 × 0.26 e$^-$ are transferred from C$^-$ to B and Al atoms, respectively, giving rise to the two $^1/_2$ π bonds; via the σ frame 0.24 e$^-$ are moving from Al to C$^-$, but practically no e$^-$ are transferred along the σ route in the BC$^-$ species. Overall, 0.60 and 0.28 e$^-$ are transferred from C$^-$ to B and Al atoms, respectively. Note that the 2s^2 (B) and 3s^2 (Al) electron distributions remain undisturbed upon the bond formation, i.e., do not participate in the bonding process, and only the 2s^2 electrons of the C$^-$ anion hybridize slightly upon bonding.

Comparing the findings of this section with those of the ground $X^4\Sigma^-$ state of the neutrals (Tables 3 and 4), we observe that the D_e's of the BC$^-$ and AlC$^-$ increase by 9.5 and decrease by 5.7 kcal/mol with a concomitant bond shortening of 0.0016 and 0.0152 Å, respectively.

At this point a comparison of the BC$^-$ and AlC$^-$ with the isoelectronic and isovalent molecules BN and AlN seems appropriate. Figure 5 presents a relative energy diagram of the BC$^-$,BN[37,39,40] and AlC$^-$,AlN[41] pairs, self-explanatory in essence; however, some remarks are in order. All four molecules are characterized by a ground state of $^3\Pi$ symmetry. But while in BC$^-$ and AlC$^-$ the $^3\Sigma^- \leftarrow X^3\Pi$ splitting is similar, i.e., 8.96

TABLE 7: Absolute Energies E (hartrees), Dissociation Energies $D_e{}^a$ (kcal/mol), Bond Lengths r_{Z-C} (Å) and r_{H-Z} (Å), Dissociation Energies D_e (kcal/mol) of the $^3\Sigma^-$ State of the HZC (Z = B, and Al) Molecules, at the CASSCF, MRCI and MRCI+Q Level. The Corresponding Values of r_{ZC} (Å) and D_e (kcal/mol) of ZC Molecules, and E (hartrees), r_{HZ} (Å), D_e (kcal/mol), μ (D), and q_Z of HZ Molecules are also Given.

method	$-E$	r_{ZC}	r_{HZ}	$D_e{}^a$ (H-ZC)	$D_e{}^b$ (HZ-C)	$D_e{}^c$ (H−Z−C)	r_{ZC}	D_e	$-E$	r_{HZ}	D_e	μ	q_Z
			HBC				BC			HB			
CASSCF	63.051550	1.4669	1.1934	83.39	97.91	168.39	1.5091	92.21	25.187583	1.2496	77.69	1.290	4.99
MRCI	63.198450	1.4503	1.1796	96.16	112.84	196.86	1.4979	100.71	25.235760	1.2336	84.19	1.384	5.01
MRCI+Q	63.2069	1.449	1.177	97.1	113.8	198.0	1.499	100.9	25.2370	1.234	84.3		
			HAlC				AlC			HAl			
CASSCF	280.278464	1.9424	1.5881	38.41	41.30	106.66	1.9802	68.25	242.509632	1.6705	68.25	−0.079	12.78
MRCI	280.415728	1.9339	1.6014	48.59	53.47	126.08	1.9710	77.49	242.549948	1.6530	72.93	−0.109	12.76
MRCI+Q	280.4252	1.934	1.601	49.4	54.7	127.3	1.973	77.9	242.5512	1.653	72.7		

[a] HZC → H + ZC. [b] HZC → HZ + C. [c] Atomization energy, HZC → H + Z + C.

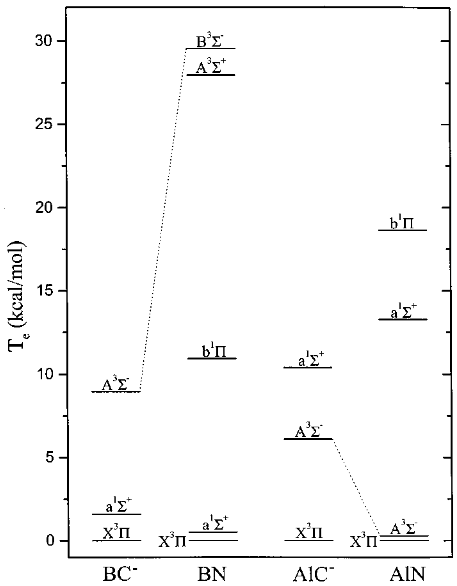


Figure 5. Relative energy diagram of the isoelectronic and isovalent pairs BC^-, BN, and $AlC-$ AlN.

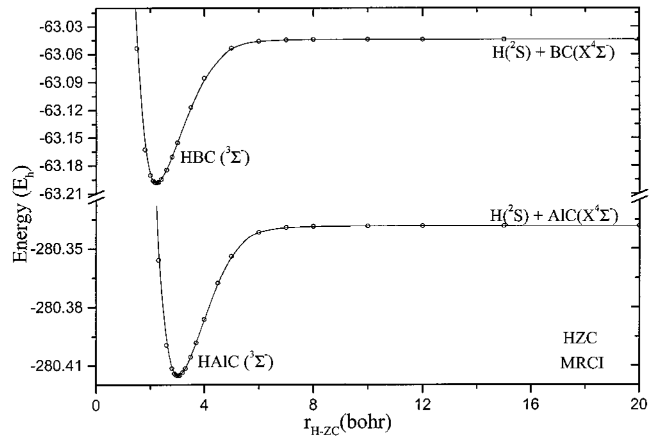


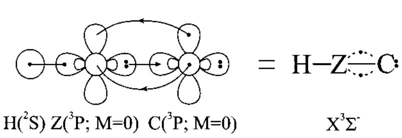
Figure 6. Potential energy curves, E vs r_{H-BC} of the HBC ($X^3\Sigma^-$) and E vs r_{H-AlC} of the HAlC ($X^3\Sigma^-$) molecules at the MRCI level.

TABLE 8: Dipole Moments μ (D) and Number of Electrons Ne_c, Ne_B, Ne_{Al}, and Ne_H, on C, B, Al, and H Atoms, of the HBC and HAlC Molecules, at the CASSCF, MRCI Level

method	μ	Ne_C	Ne_B	Ne_H	μ	Ne_C	Ne_{Al}	Ne_H
		HBC				HAlC		
CASSCF	2.704	6.27	4.77	0.97	3.517	6.55	12.24	1.21
MRCI	2.903	6.26	4.79	0.95	3.487	6.57	12.23	1.20

and 6.06 kcal/mol, the same does not hold in BN and AlN, the corresponding splittings being 29.54 kcal/mol (experiment),[40] and 0.29 kcal/mol (theory).[41] As a matter of fact, it is not certain if the $^3\Pi$ is the ground state of AlN, the $^3\Sigma^-$ being so close.[41,14] Now the $a^1\Sigma^+$ states of the BN and AlN *are not* analogous to the $a^1\Sigma^+$ states of BC^- and AlC^-, because the latter correlate to B^-,Al^- + C, while the former to B, Al + N. Finally, the bonding in the $X^3\Pi$ state of BC^- and BN[37] and AlC^- and AlN[41] is similar; the same holds for the $^3\Sigma^-$ state of BC^-, AlC^-, and BN,[39] AlN,[41] respectively.

3.4. H−BC and H−AlC Systems. With the purpose of corroborating the bonding structures of the $X^4\Sigma^-$ state of BC and AlC (schemes I and II, sections 3.1 and 3.2), we have also investigated the electronic structures of the hydrogenated species H−BC and H−AlC, at the MRCI/[(cc-pVQZ)$_H$/(cc-pV5Z-h)$_{B,C}$], and MRCI/[(cc-pVQZ)$_H$/(aug-cc-pVQZ)$_{Al,C}$] level of theory. Approaching the H(^{2}S) atom from the B and Al side of the BC and AlC molecules ($X^4\Sigma^-$ state), and taking into account the bonding Schemes I and II, the (linear) ground states are expected to be of $^3\Sigma^-$ symmetry and described pictorially by the following vbL icon (Z = B or Al). Figure 6 shows PECs of H−BC and



H−AlC, keeping the B−C and Al−C bond distances constant in their equilibrium values of the HBC and HAlC. At the MRCI level we have calculated the H-ZC, and HZ-C dissociation energies, the HZC($^3\Sigma^-$) → H(^{2}S) + Z(^{2}P) + C(^{3}P) atomization energies, equilibrium geometries, and dipole moments of the $^3\Sigma^-$ HZC state(s), Tables 7 and 8. The dominant CASSCF CF and atomic Mulliken populations are (H/Z/C)

$$\text{HZC:}\quad |\tilde{X}^3\Sigma^-\rangle \sim 0.97|1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^1\, 1\pi_y^1\rangle,\quad Z = B, Al$$

$$\text{HBC:}\quad 1s^{0.96}/2s^{0.99}2p_z^{0.84}\, 2p_x^{0.42}\, 2p_y^{0.42}/2s^{1.66}2p_z^{1.41}\, 2p_x^{0.57}2p_y^{0.57}$$

$$\text{HAlC:}\ 1s^{1.20}/3s^{1.01}3p_z^{0.64}\, 3p_x^{0.21}\, 3p_y^{0.21}/2s^{1.91}2p_z^{1.08}\, 2p_x^{0.75}\, 2p_y^{0.75}$$

Without doubt, in both molecules the HZ-C bonding is composed of two half π bonds and one σ bond. In the HBC system 2 × 0.42 e$^-$ are transferred from C to B via the π frame, and 1.1 e$^-$ (=1.41−0.34) return to C through the σ frame; analogously, in the HAlC molecule, ∼2 × 0.21 e$^-$ are moving from C to Al via the π system, while 1 e$^-$ returns to C through the σ route. Overall atomic distributions are given in Table 8. Notice that while in HBC the H atom is slightly positively charged (∼+0.05 e$^-$), in HAlC carries a negative charge of 0.20 e$^-$, in practical agreement with corresponding Mulliken charges in the B−H and Al−H ($^1\Sigma^+$) hydrides at the same level of theory (Table 7).

Dissociation energies and bond distances of H−BC and H−AlC are 96.16, 48.59 kcal/mol and 1.1796, 1.6014 Å, respectively as compared to 84.2, 72.9 kcal/mol and 1.2336, 1.6530 Å in B−H and Al−H diatomics (Table 7). (Corresponding experimental ground state values of B−H and Al−H are D_e = 82.25,[2] 72.9 ± 0.2 kcal/mol,[42] and r_e = 1.2324,[2] 1.6478 Å,[2] respectively.)

Finally, dissociation energies and bond distances of HB−C and HAl−C are 112.84, 53.47 kcal/mol and 1.4503, 1.9339 Å, respectively as compared to 100.71, 77.49 kcal/mol, and 1.4979, 1.9710 Å in BC and AlC, at the same level of theory, Tables 7, 3, and 4.

4. Synopsis and Remarks

The present work investigates the ground electronic structure of the carbides BC and AlC, the ground and the first two excited states of the corresponding anions, BC^- and AlC^-, and the ground (linear) structures of the hydrides H−BC and H−AlC, employing large correlation consistent basis set and multireference variational methods. In particular, for the neutral BC molecule we have used a series of increasing size basis sets, the largest of which, aug-cc-pCV5Z, contains 362 contracted spherical Gaussian functions. For both the neutral diatomics and their anions we have obtained PECs, D_e's, r_e's, and spectroscopic constants, and we have tried to interpret their bonding mechanism. The main findings of this report can be condensed as follows:

1. The ground state of BC and AlC is of $^4\Sigma^-$ symmetry; $^3\Pi$ is the ground state of the anions BC^- and AlC^-.

2. At the MRCI/ aug-cc-pCVnZ, n = 2−5 CBS limit (+ scalar relativistic corrections), the D_e and r_e values of the BC molecule are 102.2 ± 0.1 kcal/mol and 1.4911 ± 0.0003 Å, in complete accord with the experimental values.

For the AlC system at the MRCI/aug-cc-pVQZ level (+ scalar relativistic corrections), D_e = 77.13 kcal/mol (but estimated D_e = ~80 kcal/mol), at variance with the experimental D_e value, the latter being smaller from the theoretical value by at least 12 kcal/mol. r_e = 1.9710 Å but correcting this value for core contraction effects, an r_e = 1.963 Å is estimated, now in fair agreement with the experimental value of 1.95503 Å.

3. Our basis set study on BC reveals that core functions are necessary for obtaining accurate values of bond distances, the effect of core basis functions being $\Delta r = -0.006$ Å at the n = 3, 4, and 5 cardinality level. On the contrary, we have found that core functions do not essentially influence binding energies, their effect being not larger by +1kcal/mol for all basis sets studied. Finally, it seems that diffuse functions ("augmented" sets) for non-Rydberg neutral systems have also a negligible effect for all properties studied if $n \geq 4$.

All properties examined as a function of basis set size n, i.e., E, r_e, D_e, μ, and ω_e, converge smoothly to their CBS limits according to the simple exponential formula used. In particular, the dipole moment μ converges to the same CBS value μ = 0.945 D for all kinds of basis sets examined.

4. The binding in the BC molecule can be described as composed of two half π and one whole σ bond; in AlC it seems that the bonding is more accurately described by two-half π bonds and one-half σ bond.

5. In BC^- and AlC^- species binding energies and bond distances of the ground $^3\Pi$ states are D_e = 118.67, 77.16 kcal/mol, and r_e = 1.4445, 1.8945 Å respectively, a significant increase over the D_e value of the BC^- as compared to BC, while practically no change in D_e is observed in going from AlC to AlC^-. In both anions the bonding is comprised of $^3/_2$ π and one σ bond.

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