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Computational Studies of Electron Affinities, Acidities, and Bond Dissociation Energies of Boron-Containing Species: The $CH_3(CH_2)_{n-1}BH_2$, $CH_2F(CH_2)_{n-1}BH_2$, and $CH_3(CH_2)_{n-1}BHF$ Series

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Computational studies of three series of boron-containing compounds, $CH_3(CH_2)_{n-1}BH_2$, $CH_2F(CH_2)_{n-1}BH_2$, and $CH_3(CH_2)_{n-1}BHF$, have been carried out to probe the structural characteristics of the parent compounds and the radicals and anions derived by loss of their terminal C−H. The energies of these species yield electron affinities, acidities, and bond dissociation energies that are explained in terms of the structural characteristics, which vary with the value of *n*. One-carbon species are considered in terms of hyperconjugative effects. The radical species with $n > 1$ reveal important structures with strong tendencies for termini to interact. Carbon 2p radicals and empty 2p boron centers interact to give a cyclic radical species for $BH_2CH_2CH_2$ and BH_2CH_2CHF and bent radicals with short distances between the termini for larger values of *n*. The bent and zigzag $BH_2(CH_2)_{n-1}CH_2$ radicals for $n \geq 3$ are quite close in energy. All anions with $n \geq 2$ are cyclic and considerably lower in energy than zigzag species. Single-point energies of parent, radical, and anionic species allow the determination of electron affinities (EA), acidities (ΔH_{acid}), and bond dissociation energies (BDE). The EAs have a noticeable break between $n = 3$ and 4, a consequence of the strain energy of the $n = 2$ and 3 anions. The ΔH_{acid} values exhibit trends also related to the strained nature of the $n = 2$ and 3 anions. The values of the terminal C−H BDEs are typical of C−H bonds with the exception of the CF-substituted series, where the somewhat smaller values indicate the C−H bond-weakening effect of fluorine substitution.

Introduction

Simple alkyl anions are either barely stable like CH_3^- [adiabatic electron affinity (EA) = ~1.8 kcal/mol] or unstable with respect to electron loss (negative EA).[1,2] The group 14 congener anion of CH_3^-, SiH_3^-, is considerably more stable, having an EA of ~32 kcal/mol. Strong silicon-induced stabilization also occurs in α-substitution of alkyl anions, as exemplified by the EAs of $(CH_3)_3CCH_2^-$ and $(CH_3)_3SiCH_2^-$ of ~5 and ~22 kcal/mol. These examples make clear that silicon, whether directly bearing a formal negative charge or located α to a carbanionic center, strongly stabilizes anions to electron loss. Our earlier study of the electron, hydride, and fluoride affinities of a series of silicon-containing species, $(CH_2)_nSiH_3$ and $CHF(CH_2)_{n-1}SiH_3$, probed the distance dependence between the carbanionic/radical and silicon centers, uncovering a number of interesting features, perhaps the most interesting of which being that the lowest energy terminal anions cyclize to give siliconates (pentacoordinate silicon anions) for $n \geq 2$ (*n* corresponds to the number of carbon atoms throughout this study).[3] The EAs obtained from the cyclic siliconates were perplexing, not just because of the huge geometry changes between their acyclic radical and cyclic anion (so-called pathological cases),[4] but because no obvious trends were explicable as *n* varied from 1 to 4.

To try to understand the silicon results better, it seemed advisable to study some simpler systems that might be related. A study of the effect of boron substitution was suggested by the large carbanion stabilizing effect by boron in $(CH_3)_2BCH_2^-$ (EA = ~40 kcal/mol) and the computationally determined EAs of BH_2 (~5−7 kcal/mol)[2,5−9] as well as other properties of boron-containing organometallics that are generally explained as effects of the empty boron 2p orbital.

Elemental boron and silicon have similar electronegativities, 1.84−2.05 for boron and 1.64−2.44 for silicon, depending on the estimation method.[10,11] Their respective covalent radii and first ionization enthalpies are 83 and 117 pm and 191.3 and 187.9 kcal/mol.[10] Boron and silicon compounds in which each is covalently bound to carbon are common, as is electron-

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(1) The National Institute of Standards and Technology (NIST) maintains the excellent Gas-Phase Ion Thermochemistry tutorial at http://webbook.nist.gov/chemistry/ion/#A.

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deficient bonding in many of their compounds.[12−20] Both elements are electrophilic, each able to expand its valence shell, boron generally to four from three and silicon to five or six from four. The resulting hypervalent species are a reflection of boron's electron deficiency (lacking an octet in its valence shell, empty 2p orbital), on the one hand, and of silicon's tendency to hypervalency caused either by accessible d orbital participation and/or σ^* orbital participation and/or three-center molecular orbital involvement, on the other.[11−21]

The computations of EAs, acidities, and bond dissociation energies (BDEs) of boron-containing compounds reported here examine boron-containing species with these properties in mind, seeking to contrast and understand differences of the species examined with earlier work on silicon-containing analogues. In addition, some remarkable structural effects, particularly of various radical species, have been discovered. These combine to be a major aspect of this report; their elucidation greatly improves our understanding of the thermodynamic properties of the boron-containing species reported. There also are practical reasons for better understanding the relationships between boron and silicon species, not the least of which may add to our understanding of doped chemical vapor deposition processes.[22]

Computational Methods

All computations were carried out using a three-step procedure (optimization, frequency, single point). Optimized molecular structures were computed without symmetry constraints using Møller−Plesset second-order perturbation theory[23] (MP2) with a 6-31++G(d,p) basis set.[24] Frequency calculations and zero-point energy corrections (ZPC) were carried out by standard techniques on the optimized structures and were used to determine that the stationary points found were local minima in almost all cases (exceptions will be noted in context). Single-point computations on the optimized structures were carried out using density functional theory (DFT) with the B3LYP exchange−correlation functional and the Dunning aug-cc-pVTZ basis.[25,26] All single-point computations were zero-point corrected. The shorthand that will be used throughout to signify these steps is B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p). Tables containing the absolute and relative energies for the species reported as well as Cartesian coordinates for these structures can be found in the Supporting Information (available free of charge via the Internet at http://pubs.acs.org). All computations were carried out using the GAMESS suite of programs[27] with MacMolPlot[28] used to visualize the molecular structures.

Results and Discussion

Electron affinities (EA), gas phase acidities (ΔH_{acid}), and bond dissociation energies (BDE) are fundamentally important in all areas of chemistry because their use in relevant thermodynamic cycles allows the determination of other important thermodynamic properties.[1,2,29,30] Our recent silicon study was undertaken to probe distance relationships between a carbon center (anionic/radical) and the perturbing effect of a tetracoordinate silicon center.[3] Informed by this work, the studies reported here began by probing a similar distance dependence for boron, recognizing that while silicon and boron have some similar properties (*vide supra*), they are different as well. Explanations for the various tendencies in silicon compounds toward (1) hypercoordination (penta and hexa), (2) increased acidities of silanols, (3) smaller bending force constants of Si−O−Si versus C−O−C bonds, (4) low barriers to pyramidal nitrogen inversion in $(R_3Si)_3N$ compounds, (5) shorter silicon-to-O, -N, and -F bond lengths, and (6) stronger bond strengths to atoms or groups attached to silicon with increasing electronegativity of the atoms or groups have been reported. While controversial, such tendencies have been attributed to either d orbital contributions, back-donations to the σ^* orbital, or ionic contributions to bonding.[11] Organoboron species have similar characteristics; their tendencies toward (1) extracoordination (tetra), (2) attenuated B−C bond lengths with unsaturated carbon group substitution, (3) increasing B−B bond lengths in H-bridged boron species that have σ-CH_3 substitution, (4) ^{11}B NMR shift correlations that depend on the number of bonded substituents bearing lone pair electrons, on the electronegativity of the attached groups, and on the nature of adjacent unsaturated substituents, (5) B−C stretching force constants that increase for unsaturated substituents, and (6) high barriers to B−C rotation in compounds such as $C_6H_5BCl_2$ have been observed.[18] These tendencies are all explained as the result of interactions between empty p orbitals on boron that are readily accessible to neighboring electron donors by σ or π donation.[18]

Computations to determine the adiabatic electron affinities, acidities, and bond dissociation energies have been carried out on a series of compounds of three structural types: unsubstituted series A, $BH_2(CH_2)_{n-1}CH_3$; CF-substituted series B, $BH_2(CH_2)_{n-1}CH_2F$; and BF-substituted series C, $BHF(CH_2)_{n-1}CH_3$. The number of carbons in each series is denoted by n, which generally varies from 1 to 4, but in series A extends to 5 and 6. The electron affinity is defined as $-\Delta H°$ for eq 1;

$$A + e^{\ominus} \rightarrow A^{\ominus} \qquad (1)$$

if $\Delta H°$ is negative, the EA is positive and the anion A^- is stable. To obtain EAs, optimized structures and energies of the $BH_2(CH_2)_n$, $BH_2(CH_2)_{n-1}CHF$, and $BHF(CH_2)_n$ radicals and their

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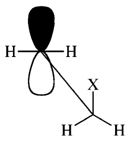
Table 1. Structural Characteristics of One-Carbon, Unsubstituted Species (series A, $n = 1$)[a,b]

bond or angle type	parent BH_2CH_3 (Å or deg) staggered structure (**1a**)	$[BH_2CH_2]^{\bullet}$ (Å or deg) planar	$[BH_2CH_2]^-$ (Å or deg)
B−H	1.19	1.19	1.22
C−H	1.09−1.10	1.08	1.09
B−C	1.56	1.53	1.47
H−B−H	118.1	119.4	115.9
H−C−H	106.4−110.2	114.1	113.0
H−B−C	120.9	120.3	122.0
H−C−B	104.2−114.5	122.9	123.5

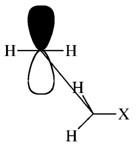
[a] Optimized at MP2/6-31++G(d,p) [b] Single values are given in cases where the bond distances or angles are equal or very nearly equal. Ranges denote more variable values that can be accessed in the Supporting Information.

corresponding anions were determined. Such adiabatic EAs are defined for computational purposes as the "difference between the total energies of the neutral and anion at their respective equilibrium nuclear configurations".[4] Acidities were obtained as the enthalpy difference between the parent molecules and their corresponding anions,[1] where a proton has been removed from the terminal carbon. The BDE studies provide energy differences between parent molecules, $BH_2(CH_2)_{n-1}CH_3$, $BH_2(CH_2)_{n-1}CH_2F$, and $BHF(CH_2)_{n-1}CH_3$, and the radicals obtained by terminal, homolytic C−H bond scission (while accounting for the hydrogen atom that is common to all of these bond scissions). These thermodynamic results will be discussed in turn after some important structural considerations obtained in the optimization studies are considered.

Structural Effects in Parent, Radical, and Anionic One-Carbon Species: Parent Compounds. The data presented in Table 1 initiate consideration of the structural effects in the three boron series (A−C). Mo, Jiao, and Schleyer (MJS) have probed some of these effects in BH_2CH_2X species as X varies widely.[31] Using an Orbital Deletion Procedure (ODP) to remove σ C−H or C−X orbital donation to the empty boron p orbital, they show that the competition between conformations where parallel C−H and C−X alignment with an empty p orbital (**1a**-staggered) and conformations where C−X or C−H are perpendicular with an empty p orbital (**1b**-eclipsed) depend on the electronegativity of X, with the hyperconjugative energy stabilization varying from 3.4 to 6.8 kcal/mol.[31] They have reported the location of two conformers for X = H, one a minimum energy structure (**1a**) and the other a transition state (**1b**), with no barrier to B−C rotation and a C−H hyperconjugative stabilization of 4.9 kcal/mol.[31] A simple interpretation of their finding that the B−C bond length is lengthened by ODP might suggest that hyperconjugation is the sole factor affecting bond lengths, but, as they point out, bond length effects are more complicated and involve steric as well as other factors, although hyperconjugation certainly is a major contribution. C−H bond lengthening in **1a** (X = H) also is reported as a measure of hyperconjugative contribution.



1a (staggered)



1b (eclipsed)

Table 2. Structural Characteristics of One-Carbon, CF-Substituted Species (series B, $n = 1$)[a,b]

bond or angle type	parent BH_2CH_2F (Å or deg) structure with C−F and B−H eclipsed	$[BH_2CHF]^{\bullet}$ (Å or deg) planar	$[BH_2CHF]^-$ (Å or deg) planar
B−H	1.18	1.18	1.21
C−H	1.10	1.08	1.09
C−F	1.42	1.35	1.44
B−C	1.56	1.52	1.45
H−B−H	120.7	122.2	119.4
H−B−C	117.4−121.9	117.8−120.0	117.5−123.2
H−C−H	106.4		
F−C−H	107.2	110.1	106.5
F−C−B	114.2	120.8	123.4
H−C−B	110.7	129.1	130.2

[a] Optimized at MP2/6-31++G(d,p). [b] Single values are given in cases where the bond distances or angles are equal or very nearly equal. Ranges denote more variable values that can be accessed in the Supporting Information.

Table 3. Structural Characteristics of One-Carbon, BF-Substituted Species (series C, $n = 1$)[a,b]

bond or angle type	parent $BHFCH_3$ (Å or deg) structure with C−H and B−F eclipsed	$[BHFCH_2]^{\bullet}$ (Å or deg) planar	$[BHFCH_2]^-$ (Å or deg) planar
B−H	1.19	1.19	1.21
B−F	1.35	1.35	1.43
C−H	1.09	1.08	1.09
B−C	1.56	1.53	1.46
H−B−F	115.8	116.9	111.5
H−C−H	105.7−109.3	115.4	114.4
F−B−C	120.3	118.8	123.0
H−C−B	109.1−113.3	122.3	121.6−124.0

[a] Optimized at MP2/6-31++G(d,p). [b] Single values are given in cases where the bond distances or angles are equal or very nearly equal. Ranges denote more variable values that can be accessed in the Supporting Information.

The calculations of BH_2CH_3 reported here are consistent with those previously reported, with the critical B−C bond length being 1.56 Å (optimized at MP2/6-31++G(d,p)) compared with the 1.57 Å reported by MJS (optimized at either HF/6-311G(d,p) or B3LYP/6-311+G(d,p)), with other very similar geometric parameters as well. There are some interesting effects of MP2 correlation. In accordance with MJS, either Hartree−Fock or density functional theory (DFT using a B3LYP functional) computations at various basis levels, imposing C_s symmetry or not, locate both the minimum structure **1a** and a transition state **1b** whose energies are identical after zero-point energy correction (no B−C barrier[31]). The shorter MP2 B−C bond length here is in accord with the MJS finding that added electron correlation shortens the B−C bond by favoring hyperconjugated structures.[31] On the other hand, various MP2/6-31++G(d,p) and MP2/6-311++G(d,p) optimizations conducted without symmetry constraints locate only a single structure in which the C−H bond and a p orbital are parallel (**1a**, X = H).

MJS have also reported that under ODP conditions the B−C bond in BH_2CH_2F is 1.59 Å for the more stable conformer (**1b** for X = F) compared with 1.57 Å when all orbital interactions are at play. This 0.02 Å effect is a complex one since the geometry of this conformer is not optimal for hyperconjugation. Our optimization studies of BH_2CH_2F at MP2/6-31++G(d,p) located only the eclipsed conformation **1b**, with a 1.56 Å B−C bond length (Table 2). We have also examined the effect of fluorine substitution on boron in $BHFCH_3$ (Table 3), where optimization yields the eclipsed conformer **1b**, with B−F and

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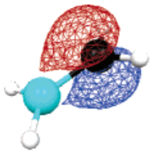
Table 4. Geometry Comparisons of $n = 2$ Radicals and Anions in Series A−C[a]

bond length/ angle (Å or deg)	$BH_2(CH_2)_n$ cyclic radical (**4**)	$BH_2(CH_2)_n$ cyclic anion	BH_2CH_2CHF cyclic radical	BH_2CH_2CHF cyclic anion	$BHFCH_2CH_2$ noncyclic radical	$BHFCH_2CH_2$ cyclic anion
B−C	1.74	1.62	1.67, to BCH_2	1.65, to BCH_2	1.57	1.60
B−C	1.74	1.62	1.80, to CHF	1.58, to CHF	2.19	1.60
C−C	1.42	1.53	1.42	1.50	1.49	1.55
C−B−C	48.0	56.6	47.9	55.3	42.7	58.0
B−C−C	66.0	61.7	71.0, to BCH_2CHF	60.1, to BCH_2CHF	91.6	61.0
B−C−C	66.0	61.7	61.1, to $BCHFCH_2$	64.5, to $BCHFCH_2$	45.7	61.0

[a] Optimized at MP2/6-31++G(d,p).

C−H eclipsed. The B−C bond length in this structure is 1.56 Å, perhaps not surprisingly, given that here too hyperconjugation is not optimal.

One-Carbon Species: Radicals and Anions. The related radicals and anionic species (Tables 1−3) that have been examined in computing the EAs possess some interesting structural features. The lowest energy radicals of $[BH_2CH_2]^•$, $[BH_2CHF]^•$, and $[BHFCH_2]^•$ all have considerable B−C bond contraction (0.03 to 0.04 Å) from their corresponding parent species, BH_2CH_3, BH_2CH_2F, and $BHFCH_3$. The B−C bond in the anions, $[BH_2CH_2]^−$, $[BH_2CHF]^−$, and $[BHFCH_2]^−$, contracts further, another 0.06 and 0.07 Å. The three radicals are all planar, suggesting that the rather large B−C bond length contractions result from electron donation to the empty boron p orbital. That effect is greater for the anions than the radicals (two-electron donation versus one). These conjectures are supported by examination of the highest occupied molecular orbitals (HOMOs) in each case. In each radical HOMO there is considerable overlap of electron density between the carbon radical center and boron, while the anion HOMOs are more dramatic, with obvious π overlap between the carbon 2p orbital and the empty 2p orbital on boron (see structures **2** and **3**). Further support comes from low-temperature EPR studies indicating that the carbon radical α to a boronate center [CH_2-BO(R)(R′)] produces a small C−B rotational barrier, as well conferring nonequivalence to the two hydrogen atoms bonded to carbon.[32]



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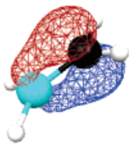
$[BH_2CH_2]^•$



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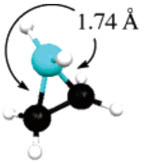
$[BH_2CH_2]^−$

Along the series from no F substitution (series A) to C−F substitution (B) to B−F substitution (C), there is no variation in the B−C bond length for the parent compounds (all are 1.56 Å), practically none for the radicals (1.53, 1.53, and 1.52 Å), and a small decrease for the anions (1.47, 1.46, and 1.45 Å). This indicates a larger effect of the species type (parent, radical, or anion) than fluorine substitution patterns (series A, series B, series C) on the B−C bond length.

The other bond length besides the B−C bonds just discussed that varies substantially is the B−H bond increase to 1.22 Å in $[BH_2CH_2]^−$, which is consistent with a negative hyperconjugative contribution (Table 1).[33] The C−F and B−F substitution patterns in $[BH_2CHF]^−$ and $[BHFCH_2]^−$ produce the same result. Once again, there is practically no C−H or B−H bond length variation on going from series A to C.

Structural Effects in Parent, Radical, and Anionic Two-Carbon Species: Parent Compounds. The parent, two-carbon compounds, $BH_2CH_2CH_3$, $BH_2CH_2CH_2F$, and $BHFCH_2CH_3$, have one structural feature of note, namely, fairly large B−C−C angles (117.7°, 114.7°, and 115.4°), although both the B−C−C and C−C−C bond angles in this study tend to be greater than might be expected in several instances. The planar BH_2 or BHF groups are slightly staggered with respect to their adjacent CH_2 and to the terminal carbon. These features are mentioned not because they are particularly notable, but because they will serve as benchmarks for various important characteristics of the related radical and anionic species.

Two-Carbon Species: Radicals. The structures of the lowest energy optimized radicals with two carbon atoms provide some surprising structural characteristics, a harbinger of interesting effects to be seen in larger radicals. Of these radicals, $[BH_2CH_2CH_2]^•$ and $[BH_2CH_2CHF]^•$ are cyclic and $[BHFCH_2CH_2]$ has a short $B−C_{terminal}$ bond length of 2.19 Å (see **4** below with B−C bond lengths of 1.74 Å).



4

$[BH_2CH_2CH_2]^•$

Typical B−C bond lengths in organoboranes are about 1.6 Å, but the B−C length in $[(C_6H_5)_4B]^−$ has been reported to be as high as 1.69 Å.[18] What is clear, no matter whether the structures are cyclic or not, is that the carbon radical and boron termini strongly interact. Other manifestations of the nature of these structures can be found in Table 4, particularly in the small internal bond angles. A shortened C−C bond length of 1.42 Å for both $[BH_2CH_2CH_2]^•$ and $[BH_2CH_2CHF]^•$ is another surprising feature; these bond lengths are ∼0.06 Å shorter than the terminal C−C bond in the other radicals we have examined including $[BHFCH_2CH_2]^•$. Furthermore, the B−C bond in $[BH_2CH_2CHF]^•$ is ∼1.67 Å, which is ∼0.1 Å longer than other B−C bond lengths in these radicals (the more typical B−C bond lengths of 1.57 Å are in line with other B−C bonds in a variety of boron organometallics[18]). Perhaps the most remarkable feature of these structures is that they have considerable eclipsing interactions, choosing these over rotating and consequently expanding the B−C−C angles. These features undoubtedly result from the sp^2 boron presenting its empty p orbital in the most favorable geometry to the terminal carbon radical, leading either to a cyclic or quite bent result.

The HOMOs of both $[BH_2CH_2CH_2]^•$ (a 17-electron system) and $[BH_2CH_2CHF]^•$ reveal B−C bonding at both B−C bonds, perhaps best described as a carbon hybridized orbital overlapping a 2p orbital of boron. Their HOMOs are very similar to that of cyclopropane (an 18-electron system) (see **5** and **6**)

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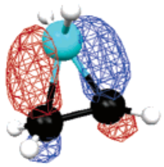
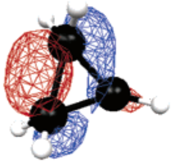
[32] Walton, J. C.; McCarroll, A. J.; Chen, Q.; Carboni, B.; Nziengul, R. *J. Am. Chem. Soc.* **2000**, *122*, 5455−5463.

[33] Schleyer, P. v. R.; Kost, D. *Tetrahedron* **1983**, *39*, 1141−1150.



5

HOMO of $[BH_2CH_2CH_2]^{\bullet}$



6

HOMO of cyclopropane

and indicate the bent-bonding nature that causes the ends to be so close. Interestingly, none of the filled MOs of $[BHFCH_2CH_2]^{\bullet}$ indicate similar B−C bonding at both B−C bonds despite its somewhat similar structure.

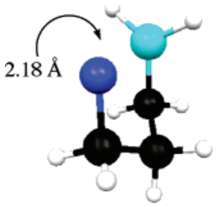
To verify that analogous cyclic silicon radicals had not been overlooked in the earlier study (although they had been sought),[3] the optimized geometries of cyclic anions, $[(CH_2)_nSiH_3]^-$, where $n = 2$, 3, and 4, were used as input for optimizations of the corresponding radicals. In the $n = 2$ and 3 cases, the ring opened, giving $[SiH_3CH_2CH_2]^{\bullet}$ and $[SiH_3CH_2CH_2CH_2]^{\bullet}$ with $Si-C_{terminal}$ distances of ∼2.8 and ∼3.3 Å. Their MOs showed no obvious interaction between the termini. Optimization of the $n = 4$ radical led to hydrogen atom loss and the formation of silacyclopentane.

Two-Carbon Species: Anions. The lowest energy optimized anions among $[BH_2CH_2CH_2]^-$, $[BH_2CH_2CHF]^-$, and $[BHFCH_2CH_2]^-$ vary structurally. For both $[BH_2CH_2CH_2]^-$ and $[BH_2CH_2CHF]^-$, an acylic, rearranged anion, $[BH_3CH{=}CHX]^-$, forms (X = H for $[BH_2CH_2CH_2]^-$ and X = F for $[BH_2CH_2CHF]^-$) by a hydride shift from the central carbon to the electron-deficient boron. The next lowest energy optimized structure for both $[BH_2CH_2CH_2]^-$ and $[BH_2CH_2CHF]^-$ and the lowest energy structure for $[BHFCH_2CH_2]^-$ is a three-membered ring formed by bond formation between the carbanionic and boron centers. Highly substituted three-membered anions have been prepared and characterized by Schuster and co-workers.[34−37] The energy difference between the rearranged and cyclic anions is ∼8 kcal/mol in series A and ∼10 kcal/mol in series B. While the rearranged structures are interesting, their connectivity is different from the optimized radical species of these series. Thus, such structures have no relevance in EA and acidity estimates that are being considered.

The geometries of the cyclic anions and the radicals just described are compared in Table 4. The cyclic anions, $[BH_2CH_2CH_2]^-$, $[BH_2CH_2CHF]^-$, and $[BHFCH_2CH_2]^-$, have B−C bond lengths of 1.62 Å, 1.65 Å (B to CH_2) (1.58 Å for B to CHF), and 1.60 Å. The B−C−C and C−B−C angles are 61.7° and 56.6° for $[BH_2CH_2CH_2]^-$, 60.1° (B−CH_2CHF) (64.5° for B−$CHFCH_2$) and 55.3° for $[BH_2CH_2CHF]^-$, and 61.0° and 58.0° for $[BHFCH_2CH_2]^-$. Each anion has a much larger C−B−C angle than its corresponding radical, but the C−C−B angles are similar. The larger C−B−C angle is not easily explained, as the radical and anion bond lengths also vary widely. The HOMO of cyclic $[BH_2CH_2CH_2]^-$ (an 18-electron system) is very similar to those depicted in **5** and **6**.

The analogous pentacoordinate, three-membered silicon anions, $[(CH_2)_2SiH_3]^-$ and $[(CH_2)_2SiH_2F]^-$, have C−Si−C bond angles that are much smaller (∼47−8°), although they span C−C bonds of roughly equal length. In the silicon anions, the Si−C bonds are considerably longer (∼1.86 Å for equatorial and ∼2.03 Å for apical) than the B−C bonds here, thus necessitating a smaller C−Si−C angle.[3] The C−Si−C angles are so much smaller than the C−B−C angles because in simple hybrid orbital terms the silicon is dsp^3 and boron is sp^3, the former more easily accommodating a small bond angle (ideally 90°) if the ligands span an apical and equatorial position.

Structural Effects in Parent, Radical, and Anionic Three-Carbon Species: Parent Compounds. Of the parent species, $BH_2CH_2CH_2CH_2F$ (**7**) has the most interesting geometric features.

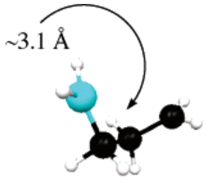


7

$BH_2CH_2CH_2CH_2F$

Its terminal fluorine is only 2.18 Å from boron, the C-to-F and C-to-B bonds are ∼6° from parallel, and the central C−C−C angle is 108.4°, all of which suggest an interaction between the 2p lone pairs of the terminal fluorine and the empty boron p orbital. On the other hand, $BH_2CH_2CH_2CH_3$ and $BHFCH_2CH_2CH_3$ have conformations with no unusual features; their central C−C−C angles are 113.0 and 112.3°.

Three-Carbon Species: Radicals. The lowest energy radical species, $[BH_2CH_2CH_2CH_2]^{\bullet}$, $[BH_2CH_2CH_2CHF]^{\bullet}$, and $[BHFCH_2CH_2CH_2]^{\bullet}$, have some structural features reminiscent of the radicals already discussed, with $[BH_2CH_2CH_2CH_{2-}]^{\bullet}$ being a particularly interesting case. One structure found has its boron and radical carbon centers at a ∼3.2 Å distance with a C−C−C angle of 111.9° (**8**, bent). The carbon radical center is slightly pyramidal, in contrast to the BH_2 terminus, which is planar like all BH_2 and BHF centers in this study. Another structure (**9**) of nearly identical energy is found in which the two termini are more distant (∼4.0 Å) and the radical has a zigzag shape, indicating no interaction between the termini. The latter structure has been found both as a second-order saddle point and as a minimum with no imaginary frequencies. The second-order species is ∼0.6 kcal/mol lower than the bent radical and ∼4 kcal/mol lower than the other zigzag structure. However, the bent radical, which is minimum, has a lower uncorrected energy by ∼0.3 kcal/mol. All attempts to find even lower energy structures that are minima have been fruitless. This raises the question of the suitability of applying zero-point corrections obtained using one basis set to single-point calculations using a different basis.



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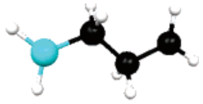

9

$[BH_2CH_2CH_2CH_2]^{\bullet}$

The structure of **8** and the lowest energy $[BHFCH_2CH_2CH_2]^{\bullet}$ are very similar. The latter has its terminal boron and carbon

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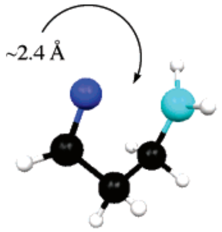
[34] Kropp, A. A.; Baillargeon, M.; Park, K. M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2155−2163.

[35] Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2149−2155.

[36] Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569−7571.

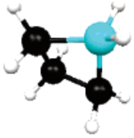
[37] Kropp, A. A.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252−6254.

centers juxtaposed at ~3.1 Å distance with a C−C−C angle of 111.8°. The two ends (planar BHF and slightly pyramidal CH_2) are twisted slightly to relieve some eclipsing interactions that are present. It seems clear that a long-range attraction between the terminal boron and carbon atoms is the controlling factor in the bent structures of both $[BH_2CH_2CH_2CH_{2-}]^\bullet$ and $[BHFCH_2CH_2CH_2]^\bullet$. What is evident is that two carbon atoms spanning the terminal sp² boron and sp² carbon atoms are not enough to allow a stronger interaction between their p orbitals, as we observed in the two-carbon radicals and will observe for $n > 3$. In the lowest energy $[BH_2CH_2CH_2CHF]^\bullet$ isomer (**10**), interaction between the fluorine lone pair electrons and the boron is indicated by the close approach of the fluorine and boron centers (~2.4 Å). This structure has its C−F and B−C bonds almost eclipsed (off by ~13°), demonstrating that the interaction between fluorine and the boron center here trumps that between the carbon radical center and boron. Interestingly, that is not the case in the two-carbon series, where the cyclic isomer is favored by ~4 kcal/mol over the isomer where fluorine and boron interact at a distance of ~3.1 Å, nor will it be the case for larger series C radicals.



10
$[BH_2CH_2CH_2CH_2F]^\bullet$

Three-Carbon Species: Anions. All the lowest energy anions among $[BH_2CH_2CH_2CH_2]^-$ (**11**), $[BH_2CH_2CH_2CHF]^-$ (**12**), and $[BHFCH_2CH_2CH_2]^-$ (**13**) are four-membered rings with fairly similar structures.



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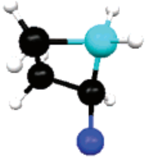

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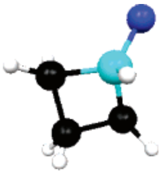

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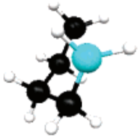
Taking a 360° sum of the internal angles as the measure of planarity, the CF-substituted ring **12** is the nearest to planar (351.3°), with the other two rings having nearly equal sums of ~348°. In these rings the C−B−C angles are 84−85°, the B−C−C angles are 85−88°, and the C−C−C angles are close to 93°. The C−C bonds are 1.54−1.55 Å and the B−C bond lengths range from 1.65 to 1.68 Å. All in all, there are no remarkable geometric differences among these rings.

Structural Effects in Parent, Radical, and Anionic Four-Carbon Species: Parent Compounds. Of the parent species, $BH_2CH_2CH_2CH_2CH_3$, $BH_2CH_2CH_2CH_2CH_2F$, and $BHFCH_2CH_2CH_2CH_3$, only $BH_2CH_2CH_2CH_2CH_2F$ has unusual geometric features, since, like $BH_2CH_2CH_2CH_2F$ (**10**), the terminal fluorine interacts with the p orbital that boron presents. The fluorine-to-boron distance is only ~2.1 Å, somewhat less than in **10** (~2.2 Å).

Four-Carbon Species: Radicals. The lowest energy radicals, $[BH_2CH_2CH_2CH_2CH_2]^\bullet$ (**14**), $[BH_2CH_2CH_2CH_2CHF]^\bullet$ (**15**), and $[BHFCH_2CH_2CH_2CH_2]^\bullet$ (**16**), all have conformations that optimize the interaction between the radical carbon center and the boron p orbital.



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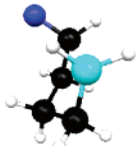

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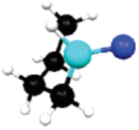
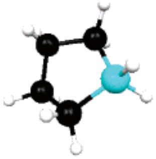


16

The B−C bond lengths are ~2.4, ~2.3, and ~2.8 Å. The BH_2/BHF faces are planar and carbon radical CH_2/CHF centers are pyramidal, with both CH_2 centers being only slightly so, but the CHF being more so. The sum of the angles about the slightly pyramidal three- and four-carbon CH_2 radicals ranges between 358.3° and 358.5°, but in $[BH_2CH_2CH_2CH_2CHF]^\bullet$, the sum of the angles is 350.7°. Additional studies of $[BH_2CH_2CH_2CH_2CH_2]^\bullet$ indicate that the bent structure (**14**) is more stable than the lowest energy zigzag structure by ~1 kcal/mol at both the corrected MP2/6-31++G(d,p)//MP2/6-31++G(d,p) and B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p) levels.

Four-Carbon Species: Anions. Each of the lowest energy four-carbon anions, $[BH_2CH_2CH_2CH_2CH_2]^-$ (**17**), $[BH_2CH_2CH_2CH_2CHF]^-$ (**18**), and $[BHFCH_2CH_2CH_2CH_2]^-$ (**19**), is cyclic.



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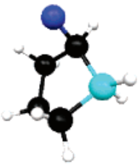

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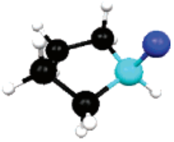


19

Not surprisingly, they deviate substantially from planarity. The most dominant feature in each ring is that the C−B−C angle is the smallest angle, easily the one deviating most from tetrahedral (~102°, ~99°, ~102° for **17**, **18**, and **19**), while the C−C−C angles in these vary from ~103° to ~108°. Nevertheless, it is clear that ring formation is dominated by both the less strained cyclic result and the powerful interaction between the carbanionic center and the empty p orbital on boron.

The corresponding zigzag $[BH_2CH_2CH_2CH_2CH_2]^-$ is more than 50 kcal/mol less stable than the cyclic species (**17**) at the B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p) level.

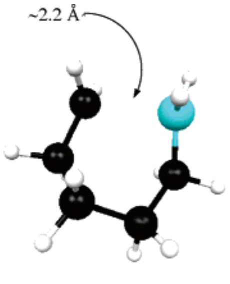
Structural Effects in Radical and Anionic Five-Carbon $[BH_2CH_2CH_2CH_2CH_2CH_2]$ and Six-Carbon $[BH_2CH_2CH_2CH_2CH_2CH_2CH_2]$ Species: Radicals and Anions. To further examine the unusual structural effects of the radical and anionic species as the number of carbons increases, a limited number of computations have been carried out on $[BH_2CH_2CH_2CH_2CH_2CH_2]$ and $[BH_2CH_2CH_2CH_2CH_2CH_2CH_2]$ radicals and anions. It seems reasonable to expect that as the carbon chain length increases, neither the BH_2 and CH_2 ends of the radicals nor the anions will "find" each other in an optimization. We have tested this by beginning optimizations both with bent structures, where the ends are close, and with zigzag inputs, where they are distant. In the case of the five- and six-carbon radicals and anions of $[BH_2CH_2CH_2CH_2CH_2CH_2]$ and $[BH_2CH_2CH_2CH_2CH_2CH_2CH_2]$, local minima of all four species have been found. Although the B-to-$C_{terminal}$ distance in $[BH_2CH_2CH_2CH_2CH_2CH_2]^\bullet$ that derives from a bent input is ~2.2 Å (**20**), the zigzag conformation is more stable by ~1 kcal/mol at the MP2/6-31++G(d,p)//MP2/6-31++G(d,p) level and ~2 kcal/mol at the B3LYP/aug-cc-pVTZ//MP2/

Table 5. Electron Affinities of $BH_2(CH_2)_n$, $BH_2(CH_2)_{n-1}CHF$, and $BHF(CH_2)_n$

$BH_2(CH_2)_n$ $n =$ (n = number of carbons)	EA[a] in kcal/mol	$BH_2(CH_2)_{n-1}CHF$ $n =$ (n = number of carbons)	EA in kcal/mol	$BHF(CH_2)_n$ $n =$ (n = number of carbons)	EA in kcal/mol
1	42.1	1	40.9	1	39.5
2	45.6	2	47.7	2	37.3
3	46.5	3	54.3[b]	3	43.6
4	61.8	4	68.2	4	58.0[c]
5	61.3				
6	61.4				

[a] EAs are computed as the difference between the zero-point-corrected single-point energies of the anion and radical. These species have been optimized at the MP2/6-31++G(d,p) level of theory, where frequency calculations and zero-point corrections have been carried out. Single-point calculations are reported at B3LYP/aug-cc-pVTZ on the optimized structures using the zero-point corrections (B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p)). [b] This EA corresponds to that between the cyclic anion and the radical having a short fluorine-to-boron bond length (**7**). The EA that corresponds with the slightly lower in energy zigzag radical is 53.4 kcal/mol. [c] This EA corresponds to that between the cyclic anion and the bent radical having a short CH_2-to-boron bond length (**16**). The EA that corresponds with the slightly lower in energy zigzag radical is 58.1 kcal/mol.

6-31++G(d,p) level. The cyclic anion, $[BH_2CH_2CH_2CH_2CH_2CH_2]^-$, is more stable than the zigzag by ~71 kcal/mol at the MP2/6-31++G(d,p)//MP2/6-31++G(d,p) level.



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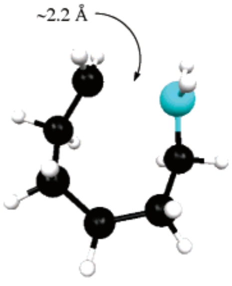

21

The $[BH_2CH_2CH_2CH_2CH_2CH_2CH_2]$ radicals and anions give similar results. The bent radical (**21**) has a B-to-$C_{terminal}$ distance of ~2.2 Å but is less stable than the lowest energy zigzag conformer by ~3 kcal/mol at B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p). The cyclic six-carbon anion is more stable than the zigzag anion by ~71 kcal/mol at MP2/6-31++G(d,p)//MP2/6-31++G(d,p).

The conformational requirements in the bent structures finally become too burdensome for larger values of n; thus the five- and six-carbon radicals are more stable in zigzag conformations and the energy favoring the zigzag over the bent conformation is widening with larger carbon number. Nevertheless, the small energy differences between zigzag and bent speak to important large interactions between the termini.

Electron Affinities for $n \geq 2$. Table 5 presents the results of EA computations of the three boron series with the complete set of $n = 1-6$ for series A and $n = 1-4$ for series B and C. A quick look at these data reveals some obvious trends that raise interesting questions about their interpretation, not to mention their comparison with the silicon study published earlier.[3] In each series a cyclic anion has been shown to be the lowest energy anion for $n \geq 2$. The corresponding EAs reveal a quite dramatic increase between $n = 3$ and 4. This is particularly evident in unsubstituted series A, where the EAs for $n = 2$ and 3 (~46 kcal/mol) are virtually identical as they are for $n = 4-6$ (~61 kcal/mol). This breakpoint also is evident for the fluorine-substituted series, but we have not carried our calculations in these series to $n = 5$ and 6. While all the anions are cyclic, some of the radicals are bent and others are zigzag. Since the energies of the radicals of various n values are very close whether bent or zigzag, the trends in the EAs presented in Table 5 are "fixed", no matter what energy values of the radicals are used. The break between $n = 3$ and 4 undoubtedly results because the energies of the anions with $n = 2$ and 3 are relatively higher than the more strain-free anions with $n = 4-6$. Thus, the three- and four-membered cyclic anions are strained relative to their larger homologues, and their EA values (the difference between the anion and radical energy) are decreased accordingly. MP2/6-31++G(d) computations of $SiH_3(CH_2)_n$ (series D) and $SiH_2F(CH_2)_n$ (series E) for $n = 2-4$ produced much more variable EAs that were difficult to rationalize on structural grounds because comparisons of species with equal n values in series D and E showed very similar structural characteristics, but quite different relative energies. There were also large geometry differences between the radicals and the cyclic anions.

Electron Affinities for $n = 1$ (BH_2CH_2, BH_2CHF, and $BHFCH_2$). The EAs of BH_2CH_2, BH_2CHF, and $BHFCH_2$ are ~42, ~41, and ~40 kcal/mol (Table 5), which indicates that the anionic species are considerably more stable than their corresponding radicals. The differences between the EAs of BH_2CH_2 and $BHFCH_2$ (~2 kcal/mol) and those between SiH_3CH_2 and SiH_2FCH_2 (~4 kcal/mol) in the previous study is small, but the magnitude of the boron EAs favors their anions relative to their radicals over the silicon species, whose EAs for SiH_3CH_2 and SiH_2FCH_2 are ~28 and ~32 kcal/mol.[3] The slightly greater EA of SiH_2FCH_2 was attributed to its anion having a greater negative hyperconjugative effect than SiH_3CH_2. No such argument can be made in the boron series, although it is reasonable that the greater magnitude of the boron EAs over the silicon ones is a reflection of a stronger negative hyperconjugative effect in the boron series because of more favorable overlap between 2p orbitals on carbon and boron.

Gas-Phase Acidities. Table 6 compiles the terminal C−H ΔH_{acid} of the parent compounds $BH_2(CH_2)_{n-1}CH_3$ for $n = 1-6$ and the fluorine-substituted series for $n = 2-4$.[38,39] Since the anions in each series are cyclic for $n > 1$, the strained smaller anions (ring sizes 3 and 4) are expected to be relatively higher in energy, as revealed earlier in the EA data. That would correspond to a break in the acidities between $n = 3$ and 4, as Table 6 records for each series. Thus, the acidities for $n = 2$ and 3 are ~363 kcal/mol while those for $n = 4-6$ are ~347−8 kcal/mol in the unsubstituted case (a ~16 kcal/mol difference). In the $BH_2(CH_2)_{n-1}CH_2F$ and $BHF(CH_2)_{n-1}CH_3$ series, there is a ~17 and ~15 kcal/mol break between $n = 3$ and 4.

Bond Dissociation Energies. Table 7 lists the terminal C−H bond dissociation energies of the parent compounds, $BH_2(CH_2)_{n-1}CH_3$, $BH_2(CH_2)_{n-1}CH_2F$, and $BHF(CH_2)_{n-1}CH_3$. In each series, the $n = 1$ BDE is smaller than $n > 1$ series members, undoubtedly because of the stabilizing radical hyperconjugative

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[38] Gordon, M. S.; Damrauer, R.; Krempp, M. *J. Phys. Chem.* **1993**, *97* (30), 7820−7822.

[39] Acidities are reported as ΔH_{acid} for the reaction $HA \rightarrow H^+ + A^-$ taking place at 0 K. These values are obtained from the zero-point-corrected B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p) and are not scaled.

Table 6. Terminal C−H Acidities (ΔH_{acid})[a] for $BH_2(CH_2)_{n-1}CH_3$, $BH_2(CH_2)_{n-1}CH_2F$, and $BHF(CH_2)_{n-1}CH_3$

number of carbons	$BH_2(CH_2)_{n-1}CH_3$ $\Delta H_{acid}{}^a$ (in kcal/mol)[38, 39]	$BH_2(CH_2)_{n-1}CH_2F$ $\Delta H_{acid}{}^a$ (in kcal/mol)	$BHF(CH_2)_{n-1}CH_3$ $\Delta H_{acid}{}^a$ (in kcal/mol)
1	361.4	352.0	366.5
2	362.9	355.5	370.2
3	363.1	354.5	366.7
4	347.3	337.9	351.8
5	347.5		
6	348.5		

[a] ΔH_{acid} values are computed as the difference between the zero-point-corrected single-point energies of the anion and parent. These species have been optimized at the MP2/6-31++G(d,p) level of theory, where frequency calculations and zero-point corrections have been carried out. Single-point calculations are reported at B3LYP/aug-cc-pVTZ on the optimized structures using the zero-point corrections (B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p)).

Table 7. Terminal C−H Bond Dissociation Energies (BDEs)[a]

$BH_2(CH_2)_{n-1}CH_3$ $n =$ ($n =$ number of carbons)	BDE[a] in kcal/mol	$BH_2(CH_2)_{n-1}CH_2F$ $n =$ ($n =$ number of carbons)	BDE[a] in kcal/mol	$BHF(CH_2)_{n-1}CH_3$ $n =$ ($n =$ number of carbons)	BDE[a] in kcal/mol
1	90.5	1	79.1	1	92.2
2	95.5	2	89.5	2	93.7
3	96.7	3	94.1[b]	3	96.5
4	96.1	4	92.4	4	96.0
5	95.8				
6	96.9				

[a] BDEs are computed as the difference between the zero-point-corrected single-point energies of the parent (e.g., $BH_2(CH_2)_nCH_3$ for unsubstituted parent) and the corresponding radical. These species have been optimized at the MP2/6-31++G(d,p) level of theory, where frequency calculations and zero-point corrections have been carried out. Single-point calculations are reported at B3LYP/aug-cc-pVTZ on the optimized structures using the zero-point corrections (B3LYP/aug-cc-pVTZ//MP2/6-31++G(d,p)). [b] This BDE corresponds to that between the parent and the radical having a short fluorine-to-boron bond length (**7**). The BDE that corresponds with the slightly lower in energy zigzag radical is 94.1 kcal/mol.

effects as discussed earlier in reference to structure **2**, where the HOMO of $[BH_2CH_2]^\bullet$ displays overlap between the 2p orbitals of carbon and boron. The HOMOs of both $[BH_2CHF]^\bullet$ and $[BHFCH_2]^\bullet$ show similar effects. In the $BH_2(CH_2)_{n-1}CH_2F$ series, all values of n give BDEs smaller than the corresponding species of $BH_2(CH_2)_{n-1}CH_3$ and $BHF(CH_2)_{n-1}CH_3$, which is consistent with other C−H BDEs of fluorine-substituted compounds. For example, the C−H BDEs in the CH_2F group of CH_3F, CH_3CH_2F, and $C_6H_5CH_2F$ are 2−3 kcal/mol smaller than the C−H BDE of the corresponding unsubstituted hydrocarbons, methane, ethane, and toluene, in both experimental and computational studies.[40−46] All of the other C−H BDEs are ∼94−97 kcal/mol, certainly in line with typical C−H BDEs.[47,48]

Conclusions

These studies have examined the structural and thermodynamic relationships in the series of boron-containing compounds, $CH_3(CH_2)_{n-1}BH_2$, $CH_2F(CH_2)_{n-1}BH_2$, and $CH_3(CH_2)_{n-1}BHF$. The one-carbon species, parent, radical, and anion, reveal interesting structural features that have been discussed in terms of hyperconjugative effects. Such effects in two of the three parent species have been studied previously.[31] Work on the radicals and anions (with the exception of BH_2CH_2, which had been studied by Schleyer and Kost)[33] is reported here for the first time and indicates the importance of hyperconjugation in radicals as well as anions.

The radical species (removal of the terminal H) with $n > 1$ have been optimized to reveal a number of important structural features, the most interesting of which is a strong tendency of the termini to interact. Such interactions between the carbon 2p radical and empty 2p boron centers dominate the structural results, giving a cyclic radical species for $n = 2$ in the unsubstituted and CF-subsituted series. Bent radicals with short distances between the termini for larger values of n have been found. In cases where $n \geq 3$ the unsubstituted radicals have bent and zigzag conformers that are quite close in energy. The anions with $n \geq 2$ are cyclic and are considerably lower in energy than any zigzag species.

The zero-point-corrected, single-point energies of the parent, radical, and anionic species have been used to compute electron affinities, acidities, and bond dissociation energies. The EA results have a noticeable break between $n = 3$ and 4, which is a consequence of the strain energy of the $n = 2$ and 3 anions relative to anions with $n > 3$. This break is present in series A, B, and C. The ΔH_{acid} values for the terminal C−H reveals trends whose origin is also the strained nature of the $n = 2$ and 3 anions. Thus, the acidities in series A, B, and C fall into two groups on either side of the $n = 3/4$ border. The values of the computed terminal C−H BDEs generally are typical of C−H bonds with the exception of the CF-substituted series B, where the somewhat smaller values indicate the C−H bond-weakening effect of fluorine substitution.

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Supporting Information Available: Tables containing the absolute and relative energies for the species reported as well as Cartesian coordinates for these structures are available free of charge via the Internet at http://pubs.acs.org.

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