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Periodic Trends in Bond Dissociation Energies. A Theoretical Study

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Bond dissociation energies (BDEs) of all possible A−X single bonds involving the first- and second-row atoms, from Li to Cl, where the free valences are saturated by hydrogens, have been estimated through the use of the G3-theory and at the B3LYP/6-311+G(3df,2pd)//B3LYP/6-31G(2df,p) DFT level of theory. BDEs exhibit a periodical behavior. The A−X (A = Li, Be, B, Na, Mg, Al, and Si) BDEs show a steady increase along the first and the second row of the periodic table as a function of the atomic number $Z(X)$. For A−X bonds involving electronegative atoms (A = C, N, O, F, P, S, and Cl) the bond energies achieve a maximum around $Z(X) = 5$. The same behavior is observed when BDEs are plotted against the electronegativity $\chi(X)$ of the atom X. Thus, for A−X bonds (A = Li, Be, B, Na, Mg, Al, Si), the BDEs for a fixed A increases, grosso modo, as the electronegativity differences between X and A increase, with some exceptions, which reflect the differences in the relaxation energies of the radicals produced upon the bond cleavage. A similar trend, albeit less pronounced, is found for single A−X bonds, where A = C, N, O, F, P, S, and Cl. However, there is an additional feature embodied in the enhancement of the strength of the A−boron bonds due to the ability of boron to act as a strong electron acceptor. The trends in bond lengths and charge densities at the bond critical points are in line with the aforementioned behavior.

Introduction

The concept of the chemical bond between two atoms was one of three fundamental postulates of classical chemistry, which in turn was properly described and interpreted by the advent of quantum theory.[1] The chemical bonds characterize the electronic structure of the molecules as well as their reactivity, and therefore their notion is of central importance. The strength of a chemical bond is reflected in its bond dissociation energy,[2] bond length, stretching frequency,[3,4] and the indirect spin−spin coupling constants between the directly linked atoms. However, the correlation between the bond "strength" and these properties is neither simple nor trivial. Only for diatomic molecules is it possible to establish a direct correlation between the strength of the bond and its bond dissociation energy.[2] In general, bond dissociation energies depend not only on the *intrinsic* or instantaneous strength of the bond but also on the stability of the radicals obtained after bond cleavage. The former is obtained by the bond scission keeping the radicals frozen. However, it is self-evident that bond fission is not a sudden event. Instead, it is followed by a reorganization of the fragments, including both the nuclear and electron relaxation. It is also important to keep in mind that redistribution of the electron density upon the bond rupture involves its drift to the separated fragments (unless they are identical), to ensure their electroneutrality[5] in the homolytic dissociations considered here. It follows as a corollary that the energy involved in the relaxation process represents very often a significant portion of the measured bond dissociation energy.

An interesting set of molecules is that including all possible single bonds between the first- and second-row atoms, which embraces all possible neutral molecules with single bonds from Li to Cl, where the remaining free valences are saturated by hydrogens. Some of these compounds, such as LiMgH or $LiAlH_2$ are unknown. Others are known as stable species, but for only 27 out of a total of 105 different substances is the experimental BDE known so far.[6−8] The scarcity of the experimental information does not enable one to develop a complete picture and to pinpoint the trend of changes in the BDEs leading to their better understanding, and therefore this can only be achieved on theoretical grounds.

Many different attempts in constructing theoretical schemes aiming to separate different energy components embodied in the BDEs are documented in the literature.[9−16] For the set of compounds mentioned above, a previous study[13] showed the good performance of the Pauling's electronegativity interpretation of covalent and ionic contributions to bonding.[1] Very recently, a theoretical analysis on the subset formed by the nonpolar bonds[17] was published. However, the periodic behavior of the BDEs of single bonds between the first- and second-row atoms had not been realized so far to the best of our knowledge. This is the main goal of the present work, where we report on high level ab initio and density functional theory (DFT) calculations of the BDEs of single bonds in molecules containing the first- and second-row atoms of the system of elements.

Computational Details

The bond dissociation energies of the 105 compounds included in our study were calculated in the framework of the G3 theory,[18] which is well suited for the treatment of radicals, yielding results of high accuracy. The standard G3 method was

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used for the whole set of the examined molecules. However, for a reduced test set of compounds involving only those with known experimental BDHs, we have also employed the G3X method,[19] based on the use of improved DFT geometries as well as the G3CC formalism.[20] In the latter scheme the final energies are obtained at the CCSD(T) level with the GT-Large basis set,[18] without using the additivity scheme inherent to the G3 method.

It is of some interest to test also the performance of the B3LYP method,[21] by comparing its results with the G3 BDE values, because this scheme is one of the most commonly used DFT computational procedures. The geometries of the studied molecules and radicals obtained by the bond cleavage were optimized at the B3LYP/6-311G(2df,p) level. Harmonic vibrational frequencies were obtained at the same level of theory to ensure that the stationary points correspond to true minima on the potential energy surface. These frequencies were used to estimate the corresponding zero point energy (ZPE). The usual scaling factor proposed in the literature for B3LYP/6-31G* frequencies is 0.98,[22] but in general, B3LYP/6-311G(2df,p) ZPE's turn out to be smaller than the B3LYP/6-31G* ones, so we have decided to use the ZPE corrections without scaling. In any case, we have verified, using all the Li containing derivatives as a test case, that BDE's obtained with scaled ZPE's differ from those obtained without scaling by less than 0.25 kJ mol^{-1}. Final energies were obtained by single point B3LYP/6-311+G(3df,2pd) calculations.

The bond critical points (bcps) were identified for all bonds undergoing cleavage by using the AIM theory,[23] because one of the parameters, which is often used to characterize the strength of a chemical bond, is the electron density at these points.[24,25] Bond critical points are stationary points of the electron density, $\rho(\mathbf{r})$, in which this magnitude is minimum along the bond path and maximum in the other two perpendicular directions. Bonding features were also examined by means of the natural bond orbital (NBO) approach.[26] The second-order NBO perturbation approach enables an estimate of the orbital interaction energies, which permit the identification of dative bonds within the system.

Results and Discussion

Calculated BDEs. The calculated BDEs are summarized in Table 1. In this table we have also included the bond dissociation enthalpies (BDHs) at 298 K to facilitate comparison with available experimental data. As shown in Figure 1, the correlation between the calculated and experimental values is very good, which gives credibility to the calculated BDHs and BDEs for the 78 compounds for which the measured values are unknown. Theoretical estimates may be also useful to anchor the experimental values, in those cases where the value is given within a large error bar (see Table 1) or when two very different experimental values have been reported.

It is worth mentioning that there is also a very good correlation between our G3 calculated values and the CBS-Q results reported previously in the literature,[17] although our estimates correlate better with the available experimental outcomes.

The correlation between the BDHs calculated at the B3LYP/6-311+G(3df,2pd)// B3LYP/6-311G(2df,p) level (abbreviated hereafter as B3LYP) and the G3 values (see Figure 2a) is also very good, as reflected by a correlation coefficient $r = 0.998$ and a slope very close to 1. However, this correlation still has a quite large intercept (−18.3 kJ mol^{-1}), which indicates a systematic difference between the B3LYP and G3 values. We noticed that this difference is close in magnitude to the high level correction term, which in the G3 theory accounts for the remaining deficiencies of the basis sets. Hence, we have added this correction to our B3LYP values, which has led to a noticeably improved correlation between B3LYP and G3 results (See Figure 2b). The slope becomes slightly closer to one and the correlation coefficient is also higher ($r = 0.999$), but more importantly the intercept is now only −1.3 kJ mol^{-1}. In summary, we conclude that the B3LYP approach, used together with the G3 HLC correction term, is a good alternative to the G3 method in estimating both BDEs and BDHs, being of almost the same accuracy but much cheaper. It is also gratifying that the differences between G3 BDEs and those calculated at the G3X and G3CC levels of theory were always negligibly small (1 kJ mol^{-1} or less) for the reduced set of molecules. This means that all BDEs are of a uniform accuracy obtained at a very high level.

Periodic Trends for Polar Bonds. Let us now analyze the possible trends in the BDHs along the periodic table. In Figure 3 the BDHs of the A−X bonds, where A is an atom belonging to the two extremes, left and right, of the first row (A = Li, Be, O, F), are depicted as a function of the X's atomic number Z(X). We shall conditionally term A as the "host" atom and X as the "substituent". The calculated BDHs exhibit an approximate, but obvious periodicity, because the trend followed by the BDHs from $Z(\mathrm{X}) = 3$ to $Z(\mathrm{X}) = 9$ is similar to that observed for "substituents" with $Z(\mathrm{X}) = 11$ to $Z(\mathrm{X}) = 17$. In other words, if we shift BDHs for the range $Z(\mathrm{X}) = 3-7$ by transformation $Z(\mathrm{X}) \rightarrow Z(\mathrm{X}) + 8$, one obtains comparable values. Hence, in what follows we are going to restrict our analysis to the first-row X atoms for the sake of brevity. It is also evident from Figure 3 that the shapes of the curves depend strongly on the electronegativity of A. The pattern found for Li and Be is substantially different from that found for O and F. Let us focus on these differences in some more detail by extending the "host" atoms A from Li to Cl.

The variations in the BDHs of AX bonds [$Z(\mathrm{A}) = 3-17$; $Z(\mathrm{X}) = 3-9$] follow two different patterns, which are presented in Figure 4a,b. For A−X bonds in which A = Li, Be, Na, Mg, Al, Si, there is a more or less steady increase in the bond energies with Z(X) as a rule, whereas for bonds in which A = C, N, O, F, P, S, and Cl, the BDHs exhibit a maximum for $Z(\mathrm{X}) = 5$, with two exceptions: the maxima for F and Cl take place at $Z(\mathrm{X}) = 4$. It is very important to note that because the standard electronegativity (χ) varies practically linearly with the atomic Z, the same behavior of the BDHs as a function of χ(X) is found. This means that for "electropositive" elements (Li, Be, Na, Mg, Al, and Si) there is an almost steady increase in the BDHs not only with the atomic numbers Z(X) of the "substituent" atom but also with its electronegativity.

A closer look at the curves in Figure 4a reveals that on going from Li to Be host atoms, there is always an increase in the binding energy, but from Be to C there is a "plateau", in the sense that despite the fact that Z(X) and its electronegativity increase, the BDHs remain almost constant. The reason behind this plateau is interesting and will be analyzed later. If one considers the concomitant variation of the electron density at the bcp for the same set of molecules (Figure 5), it is evident that it increases systematically along the first-row elements. However, boron has a quite peculiar behavior because all B−X bonds possess quite large ρ(bcp) values (vide infra).

The important finding is that although there is an increase in the bond strength, in a broad sense, associated with an increase in the electron density at the bcp, there is not a direct relationship

TABLE 1: G3 Calculated Bond Dissociation Energies (BDE, kJ mol^{-1}) and Bond Dissociation Enthalpies (BDH, kJ mol^{-1})

system	BDE	BDH	BDH(exp)
Li−Li	109.2	111.8	110.2 ± 4[a]
Li−BeH	180.4	184.2	
$\mathrm{Li{-}BH_2}$	188	192.4	
$\mathrm{Li{-}CH_3}$	193.5	199	
$\mathrm{Li{-}NH_2}$	302.4	306.7	
Li−OH	430.3	433.9	
Li−F	572.9	576.4	577 ± 21[a]
Li−Na	96.59	98.93	87.181 ± 0.001[a]
Li−MgH	152.7	155.4	
$\mathrm{Li{-}AlH_2}$	181	184.3	
$\mathrm{Li{-}SiH_3}$	214	217.4	
$\mathrm{Li{-}PH_2}$	219.8	223.5	
Li−SH	335.3	338.9	
Li−Cl	469.7	473	469 ± 13[a]
HBe−BeH	297.7	303.3	
$\mathrm{HBe{-}BH_2}$	342.3	348.6	
$\mathrm{HBe{-}CH_3}$	380.4	387.9	
$\mathrm{HBe{-}NH_2}$	503.1	509.2	
HBe−OH	613.3	618.5	
HBe−F	739	744	
HBe−Na	152.1	155.4	
HBe−MgH	233	237	
$\mathrm{HBe{-}AlH_2}$	278.7	283.8	
$\mathrm{HBe{-}SiH_3}$	319	324.3	
$\mathrm{HBe{-}PH_2}$	326.7	332.5	
HBe−SH	440.1	445.5	
HBe−Cl	558.9	563.6	
$\mathrm{H_2B{-}BH_2}$	431.6	439	
$\mathrm{H_2B{-}CH_3}$	426.8	434.9	
$\mathrm{H_2B{-}NH_2}$	583.3	592.1	
$\mathrm{H_2B{-}OH}$	626	634	
$\mathrm{H_2B{-}F}$	705.4	711.4	
$\mathrm{H_2B{-}Na}$	148	151.8	
$\mathrm{H_2B{-}MgH}$	249.3	254	
$\mathrm{H_2B{-}AlH_2}$	317.5	323.1	
$\mathrm{H_2B{-}SiH_3}$	352.6	358.1	
$\mathrm{H_2B{-}PH_2}$	362.9	370.2	
$\mathrm{H_2B{-}SH}$	466.8	474.2	
$\mathrm{H_2B{-}Cl}$	518.2	523.9	
$\mathrm{H_3C{-}CH_3}$	359.2	369.7	377.4 ± 0.8×bb[,b]
$\mathrm{H_3C{-}NH_2}$	337.7	347.3	358.6 ± 2.1[a,b]
$\mathrm{H_3C{-}OH}$	370.2	378.8	384.93 ± 0.71[a,b]
$\mathrm{H_3C{-}F}$	452	459.2	472,[a] 460.2 ± 8.4[b]
$\mathrm{H_3C{-}Na}$	139.8	144.7	
$\mathrm{H_3C{-}MgH}$	261.3	267.3	
$\mathrm{H_3C{-}AlH_2}$	335.9	342.1	
$\mathrm{H_3C{-}SiH_3}$	358.8	366.6	375.0 ± 5.0[b]
$\mathrm{H_3C{-}PH_2}$	284.1	292.7	
$\mathrm{H_3C{-}SH}$	296.7	304.5	312.5 ± 4.2[a,b]
$\mathrm{H_3C{-}Cl}$	338.1	345	350.2 ± 1.7[b]
$\mathrm{H_2N{-}NH_2}$	259.6	268.4	275.3,[a] 282[b]
$\mathrm{H_2N{-}OH}$	253.5	261.2	
$\mathrm{H_2N{-}F}$	283.6	289.6	
$\mathrm{H_2N{-}Na}$	216.9	220.2	
$\mathrm{H_2N{-}MgH}$	356.3	361	
$\mathrm{H_2N{-}AlH_2}$	456.2	463	
$\mathrm{H_2N{-}SiH_3}$	421.3	427.7	
$\mathrm{H_2N{-}PH_2}$	306.3	314	
$\mathrm{H_2N{-}SH}$	265.7	273	
$\mathrm{H_2NCl}$	246.6	252.4	
HO−OH	195.2	212.5	213.4 ± 4.2[a,b]
HO−F	194.9	199.8	
HO−Na	333.3	336.3	
HO−MgH	469.9	472	
$\mathrm{HO{-}AlH_2}$	541.2	547.4	
$\mathrm{HO{-}SiH_3}$	506.4	512.7	
$\mathrm{HO{-}PH_2}$	359.7	367.1	
HO−SH	279.1	285.6	295.4 ± 16.7[b]
HO−Cl	224.6	229.3	251 ± 13[a], 239.3[b]
F−F	151.7	155.3	158.8[a]
F−Na	478.6	481.7	477.3[c]
F−MgH	604.1	607.9	
$\mathrm{F{-}AlH_2}$	665.5	670.6	
$\mathrm{F{-}SiH_3}$	624.7	630.3	638 ± 5[b]
$\mathrm{F{-}PH_2}$	454.7	460.4	461.5 ± 10.5[b]
F−SH	336.2	340.9	
F−Cl	249.2	252.7	256.23[a]
Na−Na	87.09	89.07	73.0813 ± 0.0001[a]
Na−MgH	134.4	136.4	
$\mathrm{Na{-}AlH_2}$	155.5	158.1	
$\mathrm{Na{-}SiH_3}$	181.7	184.3	
$\mathrm{Na{-}PH_2}$	183.2	186.2	
Na−SH	285.1	288	
Na−Cl	413.4	416.1	412.1 ± 8[a]
HMg−MgH	190.4	193	
$\mathrm{HMg{-}AlH_2}$	219.9	223.3	
$\mathrm{HMg{-}SiH_3}$	250.5	254.1	
$\mathrm{HMg{-}PH_2}$	253.9	257.9	
HMg−SH	358	361.8	
HMg−Cl	479.6	483	
$\mathrm{H_2Al{-}AlH_2}$	257.9	261.8	
$\mathrm{H_2Al{-}SiH_3}$	289.4	293.2	
$\mathrm{H_2Al{-}PH_2}$	294.5	299.6	
$\mathrm{H_2Al{-}SH}$	402.5	407.9	
$\mathrm{H_2Al{-}Cl}$	502.5	507.1	
$\mathrm{H_3Si{-}SiH_3}$	313.2	318.1	310,[a] 321 ± 4[b]
$\mathrm{HSi_3{-}PH_2}$	287.3	293.1	
$\mathrm{H_3Si{-}SH}$	357.4	362.9	
$\mathrm{H_3Si{-}Cl}$	448.4	453.4	458 ± 7[b]
$\mathrm{H_2P{-}PH_2}$	225.8	231.9	256.1[b]
$\mathrm{H_2P{-}SH}$	263.7	269.7	
$\mathrm{H_2P{-}Cl}$	315.1	320.3	
SH−SH	252	257.8	276 ± 8[a], 270.7 ± 8.4[b]
SH−Cl	258.3	262.6	
Cl−Cl	234.6	237.8	242.580 ± 0.004[a]

[a] Values taken from ref 6. [b] Values taken from ref 5. [c] Values taken from ref 7.

between these two properties. The increase in the electron density is not systematically reflected in the BDHs because the relaxation effect of the radicals formed upon the bond cleavage exerts an important influence. Unfortunately, there is not an unbiased way to measure these relaxation energies. However, a reasonable estimate can be obtained by comparing the energy of the radical in its equilibrium conformation with the energy of the same radical in the frozen conformation it had in the molecule under scrutiny. In both cases the separated radicals are neutral, although they carry some effective charge in the molecules as a rule.[5] It should be also borne in mind that by keeping the conformations fixed we did not freeze the electron densities at the same time. Instead, they are optimized in both relaxed and clamped conformations. Although this picture of the relaxation is not complete, it still yields reliable information on the importance of the relaxation of the fragments on the calculated BDHs. For this purpose, we have chosen the Li−BeH, $\mathrm{Li{-}BH_2}$, $\mathrm{Li{-}CH_3}$, HBe−BeH, $\mathrm{HBe{-}BH_2}$, and $\mathrm{HBe{-}CH_3}$ compounds as suitable model systems. The energy of the BeH, BH_2, and CH_3 radicals in their equilibrium conformation was obtained at the CCSD(T)/6-311+G(3df,2p)//MP2/full)/6-311+G(d,p) level of theory. The energy of the same radicals, obtained by keeping their structure frozen as found in the different molecules, was calculated at the CCSD(T)/

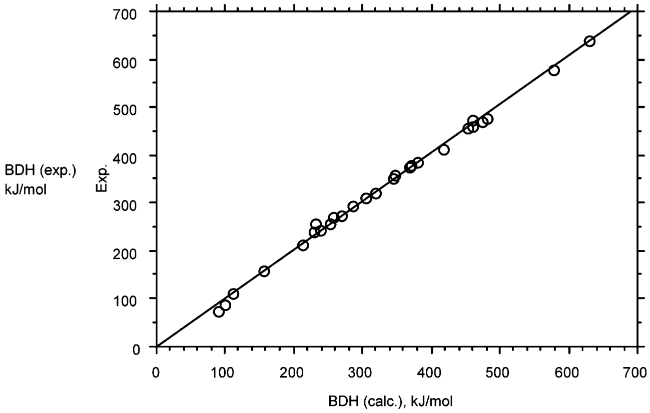

Figure 1. Comparison of theoretical and experimental bond dissociation enthalpies for the reduced set of test molecules.

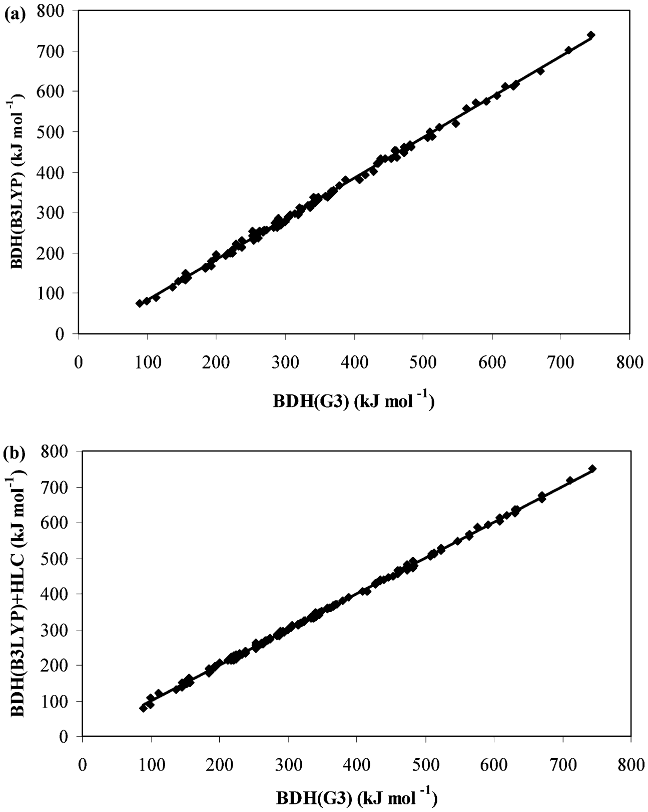

Figure 2. (a) Correlation between G3 and DFT calculated BDHs: (a) G3 vs B3LYP/6-311+G(3df,2pd); (b) G3 vs B3LYP/6-311+G-(3df,2pd) corrected by the G3 HLC additive term.

6-311+G(3df,2p) level for the sake of consistency. The results are summarized in Table 2. It is evident that the customary BDHs of Li$-$CH$_3$ and HBe$-$CH$_3$ bonds are smaller than the estimated instantaneous bond strengths, due to a stabilization of the fragment radicals after dissociation. The same effect, albeit smaller, is observed for the bonds involving the BH$_2$ group. The stabilization of the BeH groups due to relaxation is even smaller. It is also apparent that the relaxation energy also depends on the nature of the other partner in the bond, as it could be easily anticipated. The important finding, however, is that the BDHs corrected for the radicals stabilization energy steadily increase with Z(X) (and with χ(X)), thus leading to the disappearance of the plateau between Z(X) = 4 and Z(X) = 6.

It is obvious from Figure 4a that the increase in the BDHs with Z(X) for these electropositive elements is faster when Z(X) $\geq$ 7, whereas the same behavior does not hold for the charge densities at the bcp (viz. Figure 5). This is not surprising if one takes into account that the polarity of the bond increases as the substituent X approaches the end of the period, implying that there is an increase in the electrostatic stabilization due to the ionic interaction of the atoms participating in the bond. This

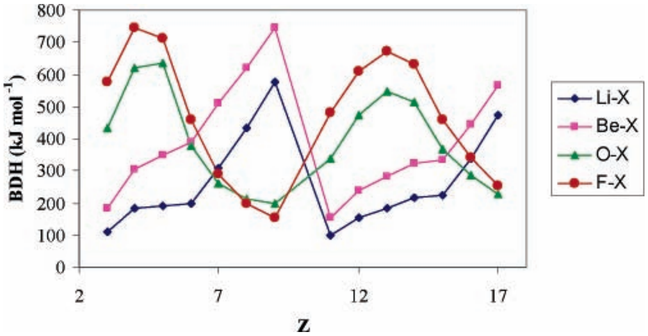

Figure 3. Variation of A$-$X BDHs (A = Li, Be, O, F) as a function of Z(X), where the "substituent" atom X belongs to the first or second row.

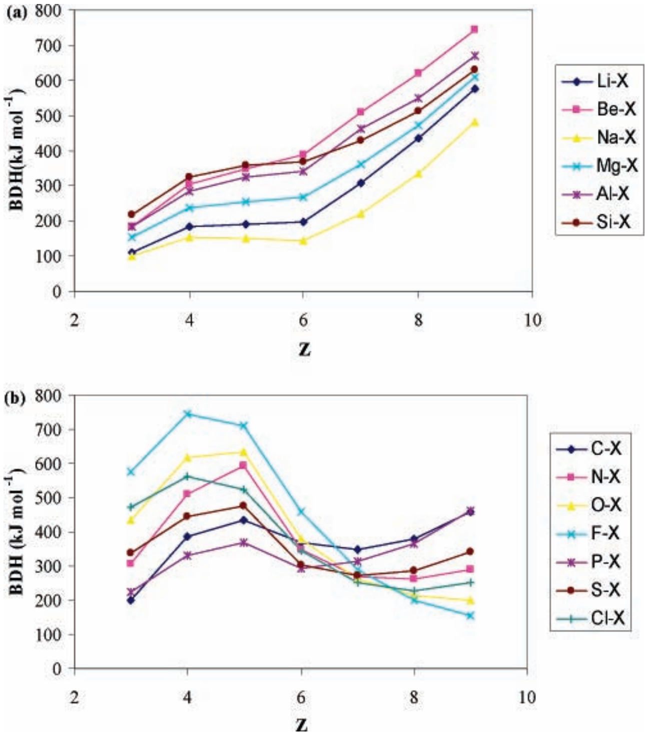

Figure 4. Variation of A$-$X BDHs as a function of the Z(X), where the "substituent" atom X belongs to the first row: (a) A = Li, Be, Na, Mg, Al, Si; (b) A = C, N, O, F, P, S, Cl, B.

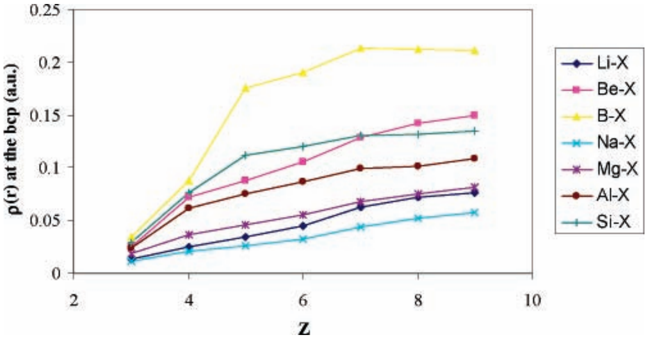

Figure 5. Dependence of the electron density ρ (bcp) of A$-$X bonds (A = Li, Be, B, Na, Mg, Al, Si) on the atomic number of the "substituent" atom, Z(X).

TABLE 2: CCSD(T)/6-311+G(3df,2p) Energies (*E*, hartrees) for BeH, BH_2 and CH_3 Radicals, Using Different Geometries and the Corresponding Relaxation Energies (ΔE, kJ mol^{-1})

	E			ΔE	
	Li derivatives	Be derivatives	equilibrium geometry	Li derivatives	Be derivatives
BeH	−15.1926463	−15.1938657	−15.1938906	3.3	0.1
BH_2	−25.8536226	−25.8568478	−25.8605182	18.1	9.6
CH_3	−39.7419645	−39.7408785	−39.7572069	40.1	42.9

effect is quite evident, for both first- and second-row atoms, if the BDHs are plotted vs the electron density at the bcp (Figure 6a,b). For atoms with $Z(X) \leq 6$ there is an almost linear increase in the BDH with the electron density at the bcp, whereas for values of $Z(X) \geq 7$ there is a sudden increase in the slope of the correlation.

Let us now analyze in some more detail the trends found in Figure 4b for more electronegative "host" elements A. The behavior of the BDHs for C−X, N−X, O−X, F−X, P−X, S−X, and Cl−X bonds as a function of *Z*(X) of the "substituent" is completely different from that found for Li−X, Be−X, Na−X, Mg−X, Al−X, and Si−X bonds illustrated earlier by Figure 4a. There is not a steady increase in the BDHs as a function of *Z*(X), but a maximum is found for $Z(X) = 5$ instead, A = F, Cl being two exceptions that give rise to a maximum at $Z(X) = 4$. It should be observed, however, that for N−X, O−X, and F−X bonds there are minima, which appear for $Z(X) = 8$ or $Z(X) = 9$. In other words, the lowest BDHs are associated with the smallest difference in the electronegativity of the directly bonded atoms. This implies that the only significant difference between the first ("electropositive") series (Figure 4a) and the second ("electronegative") series of bonds (Figure 4b), is the appearance of a maximum at $Z(X) = 5$ in the latter. Apart from this special feature, the "electronegative" series exhibits an increase in the BDEs with the difference in electronegativity of the bonded atoms, as commonly expected. This implies that any change in the electronegativity of one of the atoms participating in the bond should be reflected in the value of the corresponding BDE. This is indeed the case when the molecule becomes protonated. Proton attachment to A−X implies a significant charge depletion of the basic center and therefore an enhancement of its electronegativity that changes, as shown by Boyd et al.,[27] the BDE of the A−X bond. Interestingly, these authors found that the greater the electronegativity difference between A and X, the greater the change in the BDE due to protonation. Changes in the BDEs should also be expected in deprotonation processes, as shown by Boyd and Boyd.[28]

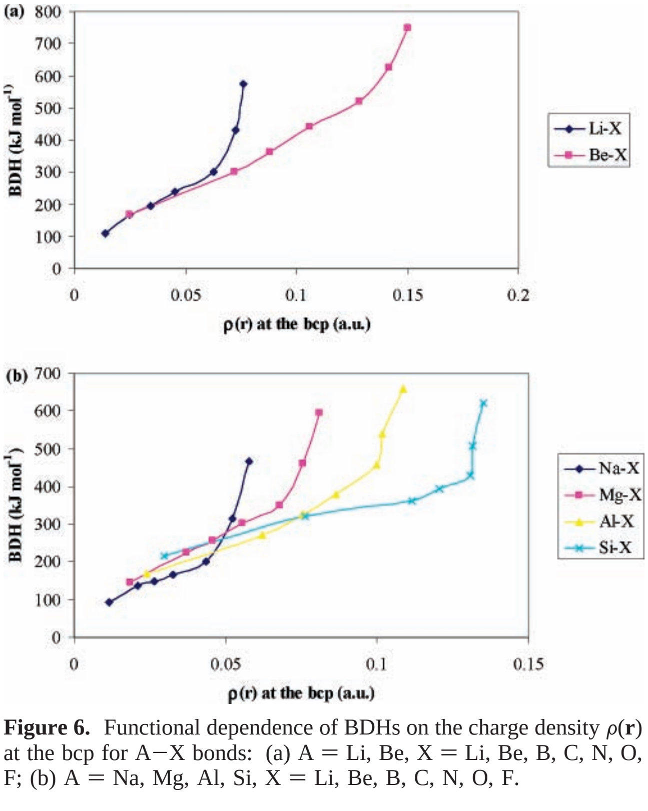

Figure 6. Functional dependence of BDHs on the charge density $\rho(\mathbf{r})$ at the bcp for A−X bonds: (a) A = Li, Be, X = Li, Be, B, C, N, O, F; (b) A = Na, Mg, Al, Si, X = Li, Be, B, C, N, O, F.

The question arises why the boron−X bonds have unexpectedly high BDHs. This is, beyond any doubt, associated with the existence of an empty valence orbital in the B atom, which favors the formation of a capto-dative bond, if the lone pair of the other vis-à-vis atom is available. The same mechanism explains the formation of the F_3B-NH_3 molecule. Actually, a second-order NBO analysis of the orbital interactions within the H_2B-CH_3 molecule reveals a charge drift from the C−H σ-bonding orbitals into the empty lone-pair orbital of boron. Of course, such capto-dative bonds are more likely to occur in molecules such as H_2B-NH_2, H_2B-OH, or H_2B-F, where the other atom in the bond has one or more electron lone pair(s). As a matter of fact, this dative interaction is so strong that the NBO analysis of these three species reveals the existence of B═N, B═O, and B═F double bonds. This result is also consistent with a very large electron density at the bcp obtained for these species (Figure 5) as mentioned above. Such behavior is in line with the fact that the BDEs of the B−C bonds in organoboranes were found to be larger than for the C−C bonds in hydrocarbons.[29] In the same paper it was also found that B−F bonds are, in general, much stronger than B−C bonds, in agreement with our previous discussion.

Finally, one should try to rationalize the fact that the BDHs of the Be atom containing compounds are systematically higher than those calculated for Li compounds. This is somewhat surprising because the electronegativity of Li is lower than that of Be. The reason is that Li−X bonds are almost completely ionic, whereas the HBe−X bonds have a non-negligible covalent character in addition to a high polarity. The NBO analysis of Li−OH shows that the system is an ionic molecule composed of Li^+ and OH^- subunits, with just a very tiny fraction of capto-dative bonding, as evidenced by the effective charge of the Li atom, which is slightly smaller than 1.0 (0.929). Conversely, a similar analysis for the HBe−OH molecule reveals the existence of a Be−O covalent bond with a strong participation of the O orbitals (4.5% Be + 95.5% O), which conclusively shows that the electron donation from oxygen to the Be atom is much more efficient than to lithium, thus leading to a stronger bond in the former case. In summary, the Be atom behaves as a good Lewis acid, yielding linkages with electron donor substituents almost as strong as those of boron. For the particular cases of F−Be and Cl−Be bonds, the BDHs are slightly larger than those of F−B and Cl−B ones, most likely due to their larger polarity.

The full set of molecules examined here exhibits a rather similar behavior if the bond lengths are examined. As shown in Figure 7a, there is a systematic (close to linear) decrease in the bond length for the electropositive "host" atoms (A = Li, Be, Na, Mg, Al, Si), following more or less the variation of the electron density at the bcp. It can be seen, however, that the increase in the BDHs observed for $Z(X) \geq 7$ is not reflected in a significant shortening of the bond. This is expected, because it is well-known that in polar covalent bonds or in ionic linkages, where the electrostatic interactions between the bonded atoms

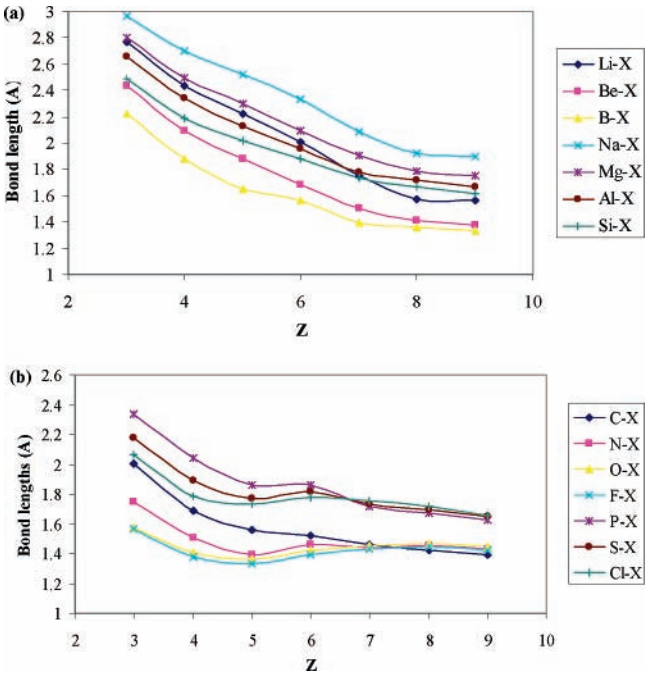

Figure 7. Functional dependence of the bond lengths of the A−X bond on Z(X), the substituent atom being a first-row element: (a) A = Li, Be, B, Na, Mg, Al, Si; (b) A = C, N, O, F, P, S, Cl.

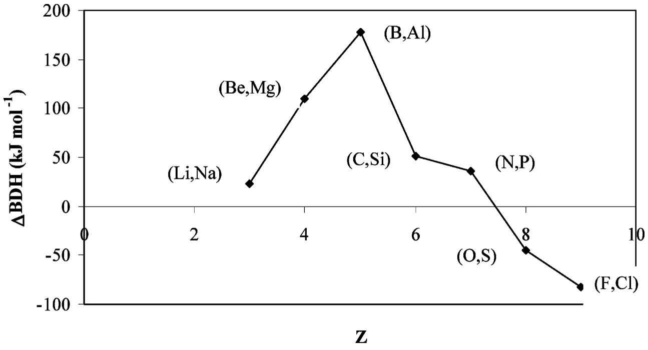

Figure 8. Differences in the BDHs (ΔBDH) of H_nA-AH_n nonpolar bonds between first-row containing compounds (A = Li to F) and second-row containing compounds (A = Na to Cl). Z is the atomic number of the first-row atom of each couple of compounds.

are large, the bond length is not a good index of the bond strength.[30]

For the electronegative “host” atoms (A = C, N, O, F, P, S, Cl), the bond lengths also decrease along the row, but a local minimum in found for Z(X) = 5 (see Figure 7b), clearly associated with the enhancement in the A−boron bonds discussed above.

Periodic Trends for Nonpolar Bonds. As mentioned in the Introduction the behavior of the BDEs of H_nA-AH_n (A = Li to F) nonpolar bonds has been fully analyzed in a recent paper,[17] so we are going to concentrate here exclusively on the comparison of the trends in the first and the second row. The difference in the BDEs of H_nA-AH_n (A = Li to F) and H_nA-AH_n (A = Na to Cl) nonpolar bonds has been plotted in Figure 8. The first conspicuous fact of this figure is that in all cases the BDE of first-row containing compounds is larger than that of second-row containing analogues, with two clear exceptions: H_2O_2 and F_2, which have a BDE smaller than their second-row counterparts: H_2S_2 and Cl_2. The unexpectedly weak bond in F_2 was discussed many times in the literature[1,31−34] and is commonly associated with the lone pair/lone pair repulsions. A recent analysis concludes[35] that the weakness of the F_2 bond is due to an unexpectedly low value of the electrostatic contribution. This conclusion is in line with the fact that F_2 is a molecule in which the Laplacian of the charge density ($\nabla^2\rho$) at the bcp is positive rather than negative, as should be expected for a normal covalent bond. A positive Laplacian indicates that the charge density in that point is smaller than in the surroundings. In other words, although the formation of a covalent bond accumulates electron density within the internuclear region, in systems such as F_2 where the atoms are very electronegative, this charge is strongly polarized toward both nuclei, weakening somehow the bond. A similar effect, although smaller should be expected for H_2O_2 and indeed $\nabla^2\rho$ at the O−O bcp is also positive. On moving from the first to the second row there is a clear decrease in the electronegativity of the atoms participating in the bond, and $\nabla\ ^2\rho$ is negative in H_2S_2 and only slightly negative in Cl_2. In summary, $\nabla^2\rho$ is more negative for first-row than for second-row H_nA-AH_n nonpolar bonds, indicating a relative higher charge concentration and therefore a stronger bond, again with two exceptions, H_2O_2 and F_2, where the opposite holds.

Concluding Remarks

Bond dissociation enthalpies of single A−X bonds involving first- and second-row atoms, from Li to Cl, where the free valences are saturated by hydrogens, exhibit periodic features characteristic for the system of elements. Here, A and X denote the “host” and “substituent” atoms, respectively. The A−X BDHs for bonds involving electropositive A atoms, namely A = Li, Be, B, Na, Mg, Al, and Si, increase along the row as Z(X) increases. On the other hand, the BDHs of bonds involving electronegative A atoms (A = C, N, O, F, P, S, Cl), attain a maximum around Z(X) = 5. This maximum is shifted to Z(X) = 4 for F and Cl atoms. The same behavior is observed if the BDHs are plotted against the electronegativity χ(X) of the substituent atom X in the A−X bond. This would imply that for molecules containing A−X single bonds involving A = Li, Be, B, Na, Mg, Al, and Si, the strength of the bond increases with the electronegativity difference between A and X, particularly if the relaxation energies of the fragments formed upon the bond cleavage are taken into account. The picture obtained for A−X single bonds where A = C, N, O, F, P, S, and Cl is more complicated, because there is a considerable enhancement in the bond strength if X = B, due to a pronounced ability of the BH_2 group to behave as a strong electron acceptor, i.e., as a strong Lewis acid. The enhanced BDHs of bonds where X = Be have the same origin. In summary, the bond strength in polar single bonds is the result of two factors: (a) the maximum overlapping between the two orbitals forming the bond, which is reflected in the charge density at the bcp and (b) the polarity of the bond, which is reflected in the shift of the bcp from the center of the bond toward the more electropositive atom.

The trends in bond lengths and charge densities at the bond critical points are in line with the aforementioned features. Thus, for A−X bonds (A = Li, Be, B, Na, Mg, Al, Si) there is a steady decrease of the bond length along the row as Z(X) increases. For A−X bonds (A = C, N, O, F, P, S, Cl) the bond lengths also decrease along the row, but they assume minima for Z(X) = 5, reflecting the highly pronounced strength of the bonds formed by the BH_2 group.

It is important to point out that BDHs predicted by the B3LYP method are in very good accordance with the G3 results provided the high level correction term (HLC) is added. It is gratifying that the latter gives a practically constant contribution to the BDHs of some 18 kJ/mol.

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