

## A THEORETICAL APPROACH TO SUBSTITUENT EFFECTS<sup>1</sup>

### INTERACTION BETWEEN DIRECTLY BONDED GROUPS IN THE ISOELECTRONIC SERIES $XNH_3^+$ , $XCH_3$ , AND $XBH_3^-$

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**Abstract**—*Ab initio* molecular orbital theory including full geometry optimization at the 4-31G level is used to examine the interactions between substituents X (X = Li, BeH, BH<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub>, OH and F) and substrates Y (Y = NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub>, BH<sub>3</sub><sup>-</sup>) in the isoelectronic series XNH<sub>3</sub><sup>+</sup>, XCH<sub>3</sub> and XBH<sub>3</sub><sup>-</sup>. The results indicate that the interaction energies are dominated by  $\sigma$ -effects. NH<sub>3</sub><sup>+</sup> is found to interact favorably with the  $\sigma$ -donors (e.g. Li, BeH and BH<sub>2</sub>) and unfavorably with the  $\sigma$ -acceptors (e.g. F, OH, NH<sub>2</sub>). The reverse pattern is observed for XBH<sub>3</sub><sup>-</sup>. The range of interaction energies for XCH<sub>3</sub> is considerably smaller than for XNH<sub>3</sub><sup>+</sup> and XBH<sub>3</sub><sup>-</sup>.

In recent publications<sup>1,3</sup> we have attempted to build up a qualitative picture of substituent interactions in a variety of systems. These have included poly-substituted benzenes<sup>1a,1d,3</sup> as well as directly bonded groups.<sup>1b,1c</sup> The key factor governing substituent interactions appears to be the difference in the electron-donating or -accepting properties of the interacting substituents: powerful electron donors interact favorably with powerful electron acceptors.

In order to assess this principle in greater detail, we have examined the interaction between substituent groups involving the first-row elements (viz. Li, BeH, BH<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub>, OH and F) with the isoelectronic substrates NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub> and BH<sub>3</sub><sup>-</sup>. Since NH<sub>3</sub><sup>+</sup> represents a powerful electron acceptor, CH<sub>3</sub> a group with fairly weak electron-donating or -accepting ability and BH<sub>3</sub><sup>-</sup> a powerful electron donor, we would hope through this study to augment our understanding of substituent interactions.

system of programs<sup>4</sup> and the 4-31G<sup>5</sup> (for H,B,C,N,O and F) and 5-21G<sup>6</sup> (for Li and Be) basis sets.<sup>7</sup> Subject to specified symmetry constraints, all structures were fully optimized using a gradient optimization technique.<sup>8</sup> Total energies (denoted 4-31G//4-31G) for XNH<sub>3</sub><sup>+</sup> and XBH<sub>3</sub><sup>-</sup> are listed in Table 1.<sup>9</sup> Corresponding optimized geometries are displayed in Figs. 1 and 2. Bond lengths are in Ångströms and bond angles in degrees. Corresponding data for XCH<sub>3</sub> are available from Ref. 10.

We were unable to obtain a satisfactory wavefunction for LiBH<sub>3</sub><sup>-</sup>. For this system, a positive eigenvalue was found for the highest occupied orbital in the 4-31G calculation. In addition, the optimized structure contained an abnormally long Li...B bond. We have therefore not included results for this system in the comparisons below.

Energies of interaction ( $E_{int}$ ) of groups X and Y may be obtained as the energy changes in the formal reactions (1):



**COMPUTATIONAL METHOD AND RESULTS**  
Standard *ab initio* molecular orbital calculations were carried out using a modified version of the Gaussian 70

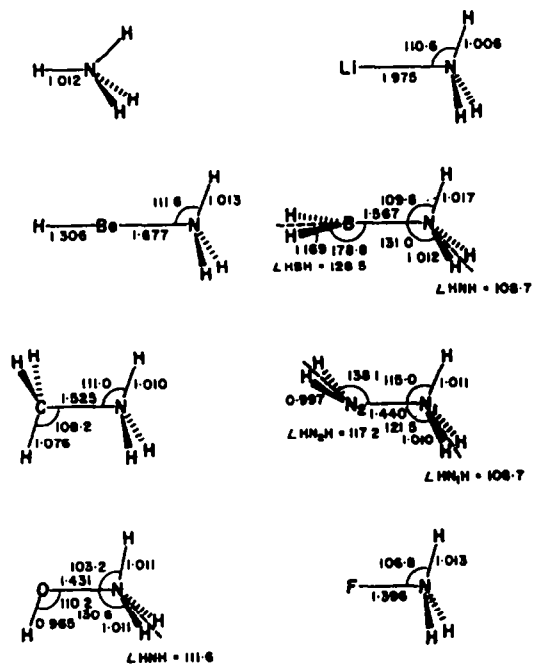
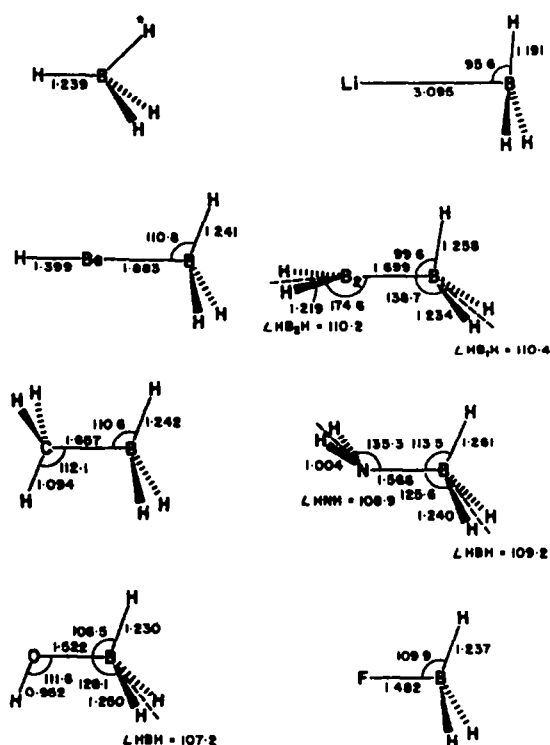
A positive  $E_{int}$  value indicates that the X-Y and H-H

Table 1. Calculated total energies (Hartrees) for 4-31G optimized structures of substituted ammonium ions (XNH<sub>3</sub><sup>+</sup>) substituted borate ions (XBH<sub>3</sub><sup>-</sup>)

X	XNH <sub>3</sub> <sup>+</sup>	XBH <sub>3</sub> <sup>-</sup>
H	-56.45888 <sup>a</sup>	-26.92454
Li	-63.41716	(-33.75519) <sup>b</sup>
BeH	-71.11785	-41.52847
BH <sub>2</sub>	-81.68881	-52.13166
CH <sub>3</sub>	-95.44076	-65.91187
NH <sub>2</sub>	-111.35666	-81.89184
OH	-131.11771	-101.72048
F	-155.06048	-125.73515

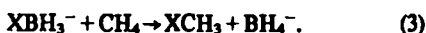
<sup>a</sup> Data taken from ref. 11.

<sup>b</sup> See text.

Fig. 1. 4-31G optimized structures for  $XNH_3^+$ .Fig. 2. 4-31G optimized structures for  $XBH_3^-$ . For  $LiBH_3^-$ , see text.

bonds are together stronger than the H-X and H-Y bonds. Since  $H_2$  is involved in the defining reactions for all the interaction energies, *relative* values of  $E_{int}$  simply compare the interaction of X and Y with the sum of the separate interactions of X with H and Y with H.  $E_{int}$  values for  $XNH_3^+$ ,  $XCH_3$  and  $XBH_3^-$  appear in Table 2.

Stabilization energies for a substituent X, bonded to either  $NH_3^+$  or  $BH_3^-$ , are defined as the energies of reaction (2) (for  $NH_3^+$ ) or (3) (for  $BH_3^-$ ).



The stabilization energies measure how effectively a substituent, X, interacts with  $NH_3^+$  (or  $BH_3^-$ ) compared to its interaction with  $CH_3$ . Positive values indicate a favorable interaction between X and either of the charged species compared to  $CH_3$ . Stabilization energies for  $XNH_3^+$  and  $XBH_3^-$  are listed in Table 3.

#### DISCUSSION

The  $E_{int}$  values listed in Table 2 indicate that interaction energies involving the groups  $NH_3^+$  and  $BH_3^-$  span a much wider range than those involving the  $CH_3$

Table 2. Interaction energies<sup>a</sup> ( $E_{int}$ , 4-31G//4-31G, kcal mol<sup>-1</sup>) for  $XNH_3^+$ ,  $XCH_3$  and  $XBH_3^-$ 

X	$XNH_3^+$	$XCH_3^b$	$XBH_3^-$
H	0.0	0.0	0.0
Li	67.6	-19.0	<sup>c</sup>
BeH	19.6	-8.1	-15.0
BH <sub>2</sub>	4.7	-8.6	-9.6
CH <sub>3</sub>	-19.5	-23.1	-16.1
NH <sub>2</sub>	-51.5	-30.1	-7.9
OH	-77.2	-31.4	8.9
F	-99.7	-26.1	31.5

<sup>a</sup> Interaction energies defined as the energy of the reaction:



<sup>b</sup> 4-31G//4-31G results for  $XCH_3$  taken from ref.10.

<sup>c</sup> See text.

Table 3. Stabilization energies<sup>a</sup> (4-31G//4-31G, kcal mol<sup>-1</sup>) for XNH<sub>3</sub><sup>+</sup> and XBH<sub>3</sub><sup>-</sup>

X	XNH <sub>3</sub> <sup>+</sup>	XBH <sub>3</sub> <sup>-</sup>
H	0.0	0.0
Li	86.6	c
BeH	27.6	-6.9
BH <sub>2</sub>	13.3	-1.0
CH <sub>3</sub>	-3.6	+7.0
NH <sub>2</sub>	-21.4	+22.2
OH	-45.8	+40.3
F	-73.6	+57.6

<sup>a</sup> Stabilization energies defined as the energy of the reaction:



<sup>b</sup> Stabilization energies defined as the energy of the reaction:



<sup>c</sup> See text.

group. Thus for NH<sub>3</sub><sup>+</sup> the range extends from +67.6 to -99.7, for BH<sub>3</sub><sup>-</sup> from +31.5 to -15.0 while for CH<sub>3</sub> the corresponding range is from -8.1 to -31.4 kcal mol<sup>-1</sup>. This difference reflects the powerful electron transfer properties of NH<sub>3</sub><sup>+</sup> and BH<sub>3</sub><sup>-</sup> compared to CH<sub>3</sub>. Thus NH<sub>3</sub><sup>+</sup>, a powerful electron acceptor, tends to interact particularly favorably with electron donors (e.g. Li) while interacting particularly unfavorably with electron acceptors (e.g. F). For BH<sub>3</sub><sup>-</sup> the reverse pattern is observed. CH<sub>3</sub>, being an intrinsically weak electron donor or acceptor does not interact strongly with either donors or acceptors and hence the small E<sub>int</sub> range.

An alternative means of examining the interaction of substituents with NH<sub>3</sub><sup>+</sup> and BH<sub>3</sub><sup>-</sup> is to use CH<sub>3</sub> as a reference (eqns 2 and 3). Stabilization energies obtained in this way (Table 3) indicate that the electropositive groups (Li, BeH and BH<sub>2</sub>) interact favorably with NH<sub>3</sub><sup>+</sup> (as concluded from the E<sub>int</sub> values), the energies increasing in the order BH<sub>2</sub> < BeH < Li. This reflects the  $\sigma$ -electron donating ability of these groups, which increases in the same order. The electronegative groups (NH<sub>2</sub>, OH and F) interact unfavorably with NH<sub>3</sub><sup>+</sup>, with the stabilization energies increasing (becoming less negative) in the order F < OH < NH<sub>2</sub>. Again this order reflects the decreasing electronegative character of the substituents along the series. For BH<sub>3</sub><sup>-</sup> the reverse pattern is obtained. BH<sub>3</sub><sup>-</sup> interacts unfavorably with the electropositive groups and favorably with the electronegative groups.

Inspection of Table 3 indicates that the range of stabilization energies observed for NH<sub>3</sub><sup>+</sup> for the substituents studied (160 kcal mol<sup>-1</sup>) considerably exceeds the corresponding range for BH<sub>3</sub><sup>-</sup> (65 kcal mol<sup>-1</sup>). This effect may be attributed to the relative lengths of N-X and B-X bonds in XNH<sub>3</sub><sup>+</sup> and XBH<sub>3</sub><sup>-</sup>. The data in Figs. 1 and 2 reveal that the N-X bonds are invariably shorter than the corresponding B-X lengths. It is these shorter N-X lengths which are apparently responsible for ac-

centuating the substituent effects (both favorably and unfavorably).

It is of interest to establish whether the charge transfer from X to Y in the system X-Y takes place through the  $\sigma$ - or  $\pi$ -system. In principle, a group of the type AH<sub>3</sub> may act either as a  $\pi$ -donor or a  $\pi$ -acceptor since it possesses two degenerate occupied  $\pi$ (AH<sub>3</sub>) orbitals (which may act as  $\pi$ -donors) as well as two degenerate vacant  $\pi^*$ (AH<sub>3</sub>) orbitals (which may act as  $\pi$ -acceptors). Mulliken charges for XNH<sub>3</sub><sup>+</sup>, XCH<sub>3</sub>, and XBH<sub>3</sub><sup>-</sup> for X = Li, BeH and F (for which a separation into  $\sigma$ - and  $\pi$ -components is possible) are listed in Table 4. Positive values indicate electron transfer from the AH<sub>3</sub> group to the substituent X.

The data indicate that  $\sigma$ -charge transfer is almost always considerably greater than  $\pi$ -charge transfer. This suggests also that interaction energies are largely determined by the  $\sigma$ -component of the total charge transfer. Only for HBeBH<sub>3</sub><sup>-</sup>, which constitutes a particularly effective  $\pi$ -transfer system (HBe is a good  $\pi$ -acceptor, while BH<sub>3</sub><sup>-</sup> is a good  $\pi$ -donor) but a poor  $\sigma$ -transfer system (both are generally  $\sigma$ -donors, though here HBe acts as an acceptor) are the  $\sigma$ - and  $\pi$ -charge transfers of similar magnitude.

The relative  $\pi$ -donating abilities of NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> (i.e. positive hyperconjugation) are reflected in the  $\pi$ -charge acceptance by BeH (Table 4). The values increase in the order NH<sub>3</sub><sup>+</sup> < CH<sub>3</sub> < BH<sub>3</sub><sup>-</sup>. This is consistent with the anticipated effect of a reduced nuclear charge on the energy levels of the group orbitals. Reducing the positive charge on the central atom is expected to raise the energy of both occupied orbitals (making these better donors) and unoccupied orbitals (making these worse acceptors). The energy levels are schematically illustrated in Fig. 3.

An intriguing point is that the  $\pi$ -donating ability of F in FY appears to increase in the order Y = NH<sub>3</sub><sup>+</sup> < CH<sub>3</sub> < BH<sub>3</sub><sup>-</sup>. This is contrary to the prediction based on

Table 4. Mulliken charges for XY for X = Li, BeH and F and Y = NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub> and BH<sub>3</sub><sup>-</sup>

X	NH <sub>3</sub> <sup>+</sup>		CH <sub>3</sub>		BH <sub>3</sub> <sup>-</sup>	
	q <sub>o</sub>	q <sub>w</sub>	q <sub>o</sub>	q <sub>w</sub>	q <sub>o</sub>	q <sub>w</sub>
Li	-0.859	+0.010	-0.502	+0.041	a	a
BeH	-0.787	+0.014	-0.441	+0.050	+0.098	+0.091
F	+0.183	-0.036	+0.523	-0.059	+0.720	-0.089

<sup>a</sup> See text.

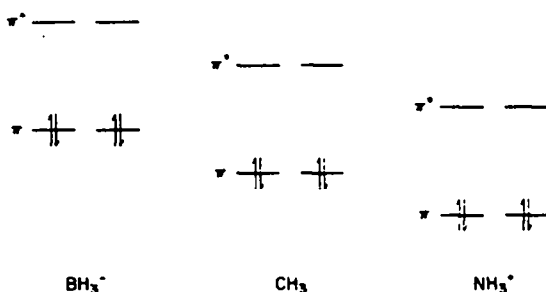


Fig. 3. Schematic representation of highest occupied orbitals and lowest unoccupied orbitals of BH<sub>3</sub><sup>-</sup>, CH<sub>3</sub> and NH<sub>3</sub><sup>+</sup> groups.

the effect of variable nuclear charge and implied by Fig. 3. However, it appears that the reversal in the expected  $\pi$ -accepting abilities of NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> stems from the drastic change in the  $\sigma$ -interaction of F within the series FNH<sub>3</sub><sup>+</sup>, FCH<sub>3</sub> and FBH<sub>3</sub><sup>-</sup>. When F is bonded to NH<sub>3</sub><sup>+</sup>, all orbitals on F are substantially lowered in energy due to the powerful electron-withdrawing effect of the NH<sub>3</sub><sup>+</sup> groups. Conversely, when F is bonded to BH<sub>3</sub><sup>-</sup>, all orbitals on F are substantially increased in energy due to the powerful electron-donating nature of the BH<sub>3</sub><sup>-</sup> group. This lowering (raising) of orbital energies by an electron-withdrawing (releasing) group has been termed a *deshielding* (*shielding*) effect,<sup>3</sup> and has been previously discussed by us in relation to substituent interactions in substituted benzenes. Thus, despite the fact that the  $\pi^*$  orbitals of NH<sub>3</sub><sup>+</sup> are lower than those of BH<sub>3</sub><sup>-</sup>, the deshielding effect of the NH<sub>3</sub><sup>+</sup> group and the shielding effect of the BH<sub>3</sub><sup>-</sup> group on the F lone pairs lead to smaller  $\pi$ -donation by F in FNH<sub>3</sub><sup>+</sup> than FBH<sub>3</sub><sup>-</sup>. Thus, the shielding effect in the series FNH<sub>3</sub><sup>+</sup>, FCH<sub>3</sub> and FBH<sub>3</sub><sup>-</sup> appears to dominate the intrinsic  $\pi$ -accepting abilities of the AH<sub>3</sub> groups.

#### CONCLUSIONS

This study confirms the intuitive expectation that XNH<sub>3</sub><sup>+</sup> systems are stabilized by  $\sigma$ -electron-donating substituents X (= Li, BeH, BH<sub>2</sub>) and destabilized by  $\sigma$ -electron-accepting substituents X (= NH<sub>2</sub>, OH, F).

The reverse results are observed for XBH<sub>3</sub><sup>-</sup>. Interaction energies for XCH<sub>3</sub> lie between those of XNH<sub>3</sub><sup>+</sup> and XBH<sub>3</sub><sup>-</sup> and span a narrower range of values. The  $\pi$ -donating abilities of the NH<sub>3</sub><sup>+</sup>, CH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> groups increase in the order NH<sub>3</sub><sup>+</sup> < CH<sub>3</sub> < BH<sub>3</sub><sup>-</sup> as expected on the basis of electronegativity arguments. On the other hand, and contrary to electronegativity arguments, the  $\pi$ -accepting abilities as reflected in results for X = F increase in the same order NH<sub>3</sub><sup>+</sup> < CH<sub>3</sub> < BH<sub>3</sub><sup>-</sup>. This result may be attributed to the deshielding effect of NH<sub>3</sub><sup>+</sup> and the shielding effect of BH<sub>3</sub><sup>-</sup> on the donor orbitals of X, leading respectively to weaker and stronger  $\pi$ -donation by X.

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