# The Influence of Hyperconjugation on Properties of Borane Adducts

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Primarily exploratory calculations, using CN/INDO methods, into the influence of hypercon-jugation on molecular properties of borane adducts are presented. Discussion centers around the molecule $BH_3CO$. While the theoretical methods are relatively crude, useful generalizations emerge which suggest the need for treatment by less approximate methods and/or suggest what experiments are likely to yield information about the concept of hyperconjugation. The properties discussed are structure, energy, nuclear spin-spin coupling, nuclear quadrupole coupling, photo-electron spectra, and infrared band intensities.

## 1. Introduction

Hyperconjugation of the $BH_3$ group has been at times a convenient concept to invoke in the rationalization of data concerning borane compounds. One approach to a systematic search for hyperconjugation has been to rank related compounds with respect to some chemical or physical property. If $\sigma$ orbital models dictate a certain ordering not borne out in the data, the $\pi$ interaction model often, but not always, provides an alternate prediction. Another approach has been to use some property of adducts with one type of Lewis acid to rank Lewis bases according to their $\pi$ acceptor abilities as an absolute quantity. Then, to establish an order of $\sigma$ donor abilities for these bases, yet another class of Lewis acid is used. These $\sigma$ and $\pi$ orders are then used for the study of $BH_3$ adducts with those same donors. For either approach, interpretation of the experimental results depends on the operation of a synergic $\sigma, \pi$ effect for amplification of $\sigma$ effects, or, in other circumstances, opposing $\sigma, \pi$ effects [1]. Often the molecules compared involve rather important chemical/structural differences such that one might wonder what confidence can be given to interpretation of the results. This problem is not easy to avoid since hyperconjugation, as the word implies, is not likely to be a dominant feature in the bonding between borane and other groups and cannot be directly studied in the absence of $\sigma$ bonding.

This communication is concerned with the results of approximate calculations on the significance to various experimental properties of $BH_3$ hyperconjugation under constrained conditions of comparison. Because of the survey nature of this study and the requisite number of calculations we have restricted the approach to use of the INDO [2] scheme of SCF LCAO MO theory. The principal value of such calculations is their comment as to whether some experimental properties are or are not significantly influenced by hyperconjugation. Consequently, the

less accurate calculations provide guidance for experimental and more accurate theoretical studies. The molecular properties to be discussed for the proto-type adduct $BH_3CO$ are: binding energies, NMR spin-spin couplings, electric field gradients, ionization potentials, geometries, dipole moments, and IR band intensities.

## 2. Methods

The theoretical methods used here are standard ones which have been treated in other places, so only a brief overview is required. The basic MO method is the INDO approximation unaltered from the original prescription [2]. The initial calculations at fixed molecular geometries used literature values for the structural parameters.

The approach used in these studies is a strictly theoretical one designed to reveal the maximum influence of hyperconjugation on molecular properties. To be specific, we compare molecular properties from calculations in which hyper-conjugation is allowed to those in which it is completely blocked. Calculations with blocked hyperconjugation were performed by the simple expedient of con-straining to null value those off-diagonal Fock matrix elements which lead to hyperconjugative interaction between the $BH_3$ and donor fragments. For the adducts considered here, symmetry factorization of $\sigma$ and $\pi$ orbitals made this technique unambiguously applicable.

The nuclear spin-spin coupling constant calculations were performed by the method of finite differences suggested [3] by Pople's group. In the interests of economy our programming uses a nuclear spin perturbation $h = 10^{-2}$ with a density convergence criterion of $10^{-6}$ to yield coupling constant errors on the order of 1 Hz. Under these conditions we obtain values for the various $J_{HF}$ of $C_2H_3F$ which are less than 0.8 Hz different from those reported [3] using a three orders tighter convergence demand.

The minimum energy geometry (restricted to $C_{3v}$ symmetry) $BH_3CO$ calcula-tions were performed by modifying the INDO program for incorporation of the STEPIT routine [4] and by using a set of driver routines based on Frost's logic in his LOCOSY program [5].

The calculation of molecular dipole derivatives for use in studying infrared band intensities for $BH_3CO$ consisted of distorting the molecule along the various symmetry coordinates defined in an earlier paper [6]. The magnitude and direction of the symmetry coordinate change is defined by the relationships between the symmetry coordinates and the internal coordinates, while the latter were changed by $\pm 0.02$ Å in the cases of bond length changes and by $\pm 2°$ in the cases of bond angle changes. Calculations were performed at $+$ and $-$ values of the symmetry coordinates to ascertain that $\mu$ changed (essentially) linearly with symmetry coordinate over the range of internal coordinate distortions given above.

## 3. Results

The initial part of this study was directed toward establishing which, if any, of several adducts treatable by the INDO scheme would show significant hyper-conjugation as judged by $\pi$ electron transfer between $BH_3$ and the donor. Table 1

Table 1. The effect of hyperconjugation on the donor $\sigma$ and $\pi$ molecular orbital populations

| Molecule | $\Delta\sigma$ base[a] | $\Delta\pi$ base[a] | $|\Delta\sigma/\Delta\pi|$ |
|---|---|---|---|
| $CH_3CO^+$ | $-0.069$ | $+0.224$ | 0.31 |
| $BH_3CO$ | $-0.063$[b] | $+0.231$[b] | 0.27 |
| $CH_3NC$ | $+0.005$ | $-0.013$ | 0.39 |
| $BH_3NC^-$ | $+0.007$ | $-0.017$ | 0.41 |
| $CH_3CN$ | $-0.016$ | $+0.046$ | 0.35 |
| $BH_3CN^-$ | $-0.014$ | $+0.044$ | 0.32 |
| $BH_3NH_3$ (eclipsed) | $+0.007$ | $-0.013$ | 0.54 |

[a] The increase in electron densities in the $a$, ($\sigma$) and $e$ ($\pi$) MO's of the donor (CO, NC$^-$, CN$^-$, NH$_3$) when hyperconjugation is permitted.
[b] The Sichel-Whitehead parametrization of CNDO gives $\Delta\sigma = -0.094$ and $\Delta\pi = 0.250$.

lists those adducts studied with the difference in fragment $\sigma$ and $\pi$ orbital populations for the normal and nohyper calculations (our preliminary calculations included some $CH_3^+$ adducts and these are also shown in Table 1). CO and $CN^-$ are the only $\sigma$ donors which also act as $\pi$ acceptors from $CH_3^+$ and $BH_3$ while the donors $NH_3$ and $NC^-$ appear as $\pi$ donors toward $CH_3^+$ and $BH_3$. The operation of synergistic charge flow between donor and acceptor is apparent for all molecules and it is of some interest that the effectiveness of the synergic interaction, as judged by the ratio $\Delta\sigma/\Delta\pi$, is greater for the $\pi$ donors (0.4–0.5) than for the $\pi$ acceptors ($\sim 0.3$). Of the donors represented in Table 1, only CO exhibits what could be termed a significant degree of $\pi$ interaction with acceptor fragments and, consequently, we restricted our further investigations to $BH_3CO$.

We feel it worth noting that the details of the synergic $\sigma/\pi$ coupling for both $\pi$ acceptors show that such coupling is not a property of the donor alone, but depends also on the acid. Therefore, conclusions based on an assumed trans-ferability of $\sigma$ donor amplification by $\pi$ acceptor behavior for a given donor may be suspect.

*Hyperconjugation and Structure.* In these calculations our interest centers mainly on the bond angles and distances about the boron. The results concerning the HBC angles and HB distances could be quite interesting because of the synergic relation between $\sigma$, $\pi$ charge flow and the predicted consequences of $\sigma$ donation and $\pi$ acceptance on these parameters. Hyperconjugatively enhanced $\sigma$ donation to $BH_3$ should increase the HBC angle whereas $\pi$ hyperconjugation itself may be argued to force planarity of the group. Hyperconjugation should, through $\sigma$, $\pi$ coupling, lead to a marked shortening of the adduct bond whereas the BH bond distance should increase.

For $BH_3CO$ (Table 2), the hyperconjugation produces a marked shortening of the B–C distance by 0.18 Å. The compensating influences of $\sigma$ donation, $\pi$ acceptance by CO on the HBC angle yields an angle change of only 0.7°, the direction of which (decrease) implies the $\pi$ interaction is of only minimally greater importance than the increased $\sigma$ donation. Finally, the expected lengthening of $r_{BH}$ is less than $10^{-2}$ Å and suggests that the BH bond distance is not appreciably influenced by hyperconjugation. Parallel results were obtained for $CH_3CO^+$.

Table 2. Energy minimum structural parameters for $BH_3CO$

| Structural parameter | norm. | $h_\pi = 0^a$ | $h_\sigma = 0^a$ |
|---|---|---|---|
| $r_{BH}$ (Å) | 1.20 | 1.20 | 1.19 |
| $r_{BC}$ (Å) | 1.45 | 1.63 | 3.51 |
| $\alpha_{HBC}$ (deg.) | 106.6 | 107.3 | 89.8 |
| $r_{CO}$ | 1.21 | 1.18 | 1.20 |

[a] $h = 0$ refers to zeroed inter-fragment interactions of $\pi$ and $\sigma$ orbitals.

Thus it appears that the BH distance and BH-donor angle are of little practical value as probes of hyperconjugative effects. For contrast, the geometry of $BH_3CO$ was energy minimized under conditions of no $\sigma$ interaction between $BH_3$ and CO. Inspection of these results (Table 2, Column 4) reveals (a) a very slight tendency for the $BH_3$ fragment to invert toward CO, (b) a very weak $BH_3$, CO interaction over a B–C distance of 3.5 Å, and (c) a marked insensitivity of the B–H distance to the presence of the CO group under any conditions of inter-action (even for free $BH_3$ the energy minimum BH distance is less than 0.01 Å different from those in Table 2).

  *Energy.* It is this molecular property for which the INDO method is expected to be least accurate. For this reason we have repeated the calculations using the CNDO parametrization scheme of Sichel and Whitehead [7] (for the energy minimum INDO structures) with the result that of the 92 kcal mole$^{-1}$ computed for $BH_3 + CO \rightarrow BH_3CO$, a net of 42 kcal mole$^{-1}$ results from the effects of including hyperconjugation. By examining the change in the contribution to the total energy from the change in B, C two-center interaction, it is apparent that the $\pi$ covalent interaction ($-68$ kcal) is of comparable importance to the change in $\sigma$ covalent interaction ($-47$ kcal) but that these interactions are not the only ones to be considered since the change in total energy is much less than their sum. While these figures for $\sigma$ and $\pi$ covalent energies are probably too large, and the $\pi$ energy overestimated relative to the $\sigma$, their values warn that neither $\sigma$ nor $\pi$ covalent bonding alone can account for the stability of $BH_3CO$. Thus, while the adduct bond energy is obviously sensitive to hyperconjugation, this sensitivity is dependent in large part to the effectiveness of $\sigma$, $\pi$ synergic coupling. To understand the relative stabilities of $BH_3$ adducts, even in the gas phase, means understanding not only the relative $\sigma$ donor and $\pi$ acceptor properties of the donors but also the relative degrees of $\pi$, $\sigma$ synergic coupling within the donor molecules.

  *Nuclear Coupling Constants.* Table 3 presents the results of the finite difference calculations of $^1J_{HB}$, $^1J_{BC}$, and $^2J_{HX}$ (X = H, C) in $BH_3CO$. As could have been anticipated, the $^1J_{HB}$ are not very sensitive to hyperconjugation ($\Delta\,^1J_{HB} \sim 2$ Hz or 2%). $^1J_{HB}$ arises only[1] from spin polarization of the $\sigma$ MO's and therefore is directly related to the $\sigma$ donor property of the base. Thus, the small change in

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  [1] In an SCF method as used here this is not strictly true. The $e$ symmetry molecular orbitals are spin-polarized also and as the $e$ and $a$ orbitals are coupled in the SCF procedure the former have an indirect effect on the latter.

Table 3. Effect of hyperconjugation on the Fermi one- and two-bond coupling of $BH_3CO$

| $^1J_{HB(Hz)}$ | | $^1J_{BC(Hz)}$ | | $^2J_{HX(Hz)}$ | |
|---|---|---|---|---|---|
| norm. | $h=0^a$ | norm. | $h=0^a$ | norm. | $h=0^a$ |
| 112.2 | 110.9 | 42.1 | 21.2 | $X=C$ | |
| | | | | $-\ 9.0$ | $-0.3$ |
| | | | | $X=H'$ | |
| | | | | $-17.1$ | $-3.9$ |

$^a$ $h=0$ signifies calculations with blocked hyperconjugation.

Table 4. Summary of $\sigma$ and $\pi$ contributions to $^2J_{HX}$ of $BH_3CO^a$

| | norm. | $h=0$ | $\Delta$ |
|---|---|---|---|
| $J_{HC}\ \sigma$ | $-\ 9.0$ | $-0.3$ | $-\ 8.7$ |
| $\pi$ | 0.0 | 0.0 | 0.0 |
| $J_{HH}\ \sigma$ | $-\ 0.6$ | $-5.5$ | $+\ 4.9$ |
| $\pi$ | $-16.6$ | 1.6 | $-18.3$ |

$^a$ All values in Hz.

$^1J_{HB}$ on admitting the $\pi$ interaction suggests that variation in $^1J_{HB}$ over a series of donors will to a good approximation reflect the variation in $\sigma$ donor properties exclusive of hyperconjugative effects[2]. Thus one is not encouraged to use this experimental quantity to attempt an assessment of the extent of hyperconjugation in $BH_3X$ compounds. The expected effect of hyperconjugation is noted for $^1J_{BC}$ and the effect is large. Similarly, hyperconjugation has a fairly important effect on the $^2J_{HX}$. The constants and their changes are analyzed[3] in Table 4 by considering separately the $\sigma$ ($a_1$ symmetry) and $\pi$ ($e$ symmetry) contributions.

The $^2J_{HC}$ is, of course, controlled by the changes in coupling via $\sigma$ orbitals so that increased $\sigma$ donation accompanying hyperconjugation increases the effectiveness of coupling between H and C. An interesting set of experiments comes to mind here. The order of $^1J_{BD}$ for a series of $R_3B \cdot D$ adducts might be used to establish an order of adduct bond $\sigma$ interactions in the relative absence of $\pi$ hyperconjugation. Comparison of these $^1J_{BD}$ with those for $H_3B \cdot D$ ... adducts could reveal, in the event of reversals, which donors exhibit inordinately large $\pi$ interaction with $BH_3$ or inordinately large $\sigma/\pi$ synergism. That $^2J_{HD}$ should parallel $^1J_{BD}$ is a relationship which could be used as a check on the appropriateness of such an interpretation.

The $^2J_{HH}$ offer a different, perhaps more useful probe as, like the $^1J_{HB}$, the coupled nuclei are located within the $BH_3$ fragment. The $\sigma$ and $\pi$ molecular orbital contributions to $^2J_{HH}$ are of comparable importance but opposite sign in the nohyper calculations, while the $\pi$ orbital contribution strongly dominates the normal

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[2] This finding lends support to the interpretation (see Ref. [1]) of $^1J_{BH}$ in a series of phosphine-borane adducts.

[3] The technique to effect such an analysis is the SCF (with finite perturbation) equivalent of the infinitesimal perturbation theory technique. See Ref. [8].

calculation. Most interesting is that the changes in $\sigma$ and $\pi$ contributions with hyperconjugation are oppositely directed (Table 4) and of large magnitude. As the two effects oppose one another with the $\pi$ clearly dominating, an understanding of $^2J_{HH}$ based on consideration of $\pi$ orbitals alone might be adequate for directly comparing hyperconjugation in related adducts.

It is important to point out that rules based on another model [9] of the $^2J_{HH}$ relation to hyperconjugation are consistent with our results. Those rules predict that $\pi$ electron withdrawal from the $BH_3$ will result in a negative shift in the $^2J_{HH}$. Applied to the $BH_3$ hyperconjugation problem these rules correctly predict the calculated shift in $^2J_{HH}$ (note, however, the rules incorrectly suggest that the $\sigma$ and $\pi$ changes will be similarly directed). The results in Table 4 show the $\pi$ changes to be the same as those predicted and dominating the $\sigma$ changes.

Entirely parallel results, which serve to generalize the $BH_3CO$ results, have been obtained for calculations with $CH_3CO^+$ and $CH_3CN$.

*Field Gradients.* For $BH_3$ adducts one finds the possibility of studying hyperconjugation using the $B$ nuclear quadrupole as a probe. From these calculations we find the assymmetry in boron $p$ orbital populations to be markedly influenced by hyperconjugation; $f_z(\equiv q_\sigma - \frac{1}{2}q_\pi)$ [10] has the value $-0.262$ for nohyper and decreases to $-0.099$ with hyperconjugation. $\pi$ back donation by $BH_3$ tends to make $q_\pi$ smaller in magnitude while $q_\sigma$ is increased; together, these changes result in a more symmetric $p$ orbital charge distribution for $B$. Using $q_{at} = -2.09 \times 10^{15}$ esu cm$^{-3}$ for boron [10], these $f_z$ values correspond to $e^2Qq$ values of 1.409 MHz and 0.532 MHz, respectively. To estimate the effects of other atom charges on the boron-field gradient, we adopted a point charge model to find the other atom charge contributions to the boron field gradient to be only slightly affected by hyperconjugation: 0.486 MHz without and 0.41 MHz with hyperconjugation. Interestingly, it is the carbon atom charge which dominates the other-atom contributions in both the normal and no hyper cases but off-setting changes in carbon versus the three hydrogen atom charges cause the small dependence of $e^2Qq$ on other-atom contributions. That is to say, some 25% of the boron field gradient is due to the other-atom contributions, but the variation in $q_B$ with hyperconjugation is due almost exclusively to variation in charge density in the boron valence orbitals. At this point we might be optimistic about the use of $^{11}B$ quadrupole coupling as a means of detecting $BH_3$ hyperconjugation in a series of adducts of related donors. Again, an order of $\sigma$ donor strengths toward boron, established for $BR_3$ adducts with no hyperconjugation, would be helpful. As with the $^2J_{HX}$, hyperconjugation exerts an influence on $e^2Qq$ predominantly through the coupling of charge flow between $\pi$ and $\sigma$ orbitals, rather than through the $\pi$ orbitals directly (to the extent that the $-0.89$ MHz shift in $e^2Qq$ that arises from the boron valence shell results from a contribution of $-0.81$ MHz from increased $\sigma$ donation but only $-0.07$ MHz from changes in $\pi$ bonding). Thus a different order of $^{11}B\,e^2Qq$ for $BH_3$ adducts than for $BR_3$ adducts might identify the operation of hyperconjugation.

*Photoelectron Spectroscopy.* Photoelectron spectroscopy is another technique of potential use in studying or identifying the role of hyperconjugation in borane adducts. By assuming the validity of Koopmans' theorem, the shifts in eigenvalues

of the $a_1$ (BH$_3$) and $e$ (BH$_3$) orbitals may be examined for sensitivity to hyper-conjugation. Our CNDO calculations, using the Sichel/Whitehead scheme [7] for BH$_3$CO, suggest that the BH$_3$ molecular orbital of $e$ symmetry is stabilized by hyperconjugation by about 0.25 eV. The $a_1$ orbital is destabilized by about 0.2 eV. These changes are in the expected directions but appear to be too small to be of much value in diagnosing the occurrance of hyperconjugation. Inspection of the $a_1$ orbital eigenvectors reveals it to be a severe approximation to view this orbital as a "BH$_3$" MO as it is a highly delocalized orbital. Consequently, the energy of this orbital is in large part determined by the nature of the donor. Only in closely related series of adducts would splitting between the $e$ and $a_1$ ionization potentials, as well as the individual shifts, be a conceivable value for the identification and study of hyperconjugation.

*Intensities of Infrared Bands.* Of the 8 distinct symmetry coordinates for this molecule only five are inherent to the BH$_3$ group (2 from the $a_1$ symmetry set and 3 from the $e$ symmetry set). To analyze the $a_1$ dipole derivatives, we have made use of the expressions [11]:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{sp} + \sum_\alpha q_\alpha \cdot \boldsymbol{r}_\alpha,$$

$$\varDelta \boldsymbol{\mu} = \varDelta \boldsymbol{\mu}_{sp} + \sum_\alpha (\varDelta q_\alpha \cdot \boldsymbol{r}_{\alpha(f)} + q_{\alpha(i)} \cdot \varDelta \boldsymbol{r}_\alpha)$$

where we have used the dipole expression appropriate to the INDO scheme ($\alpha$ runs over all atoms, and the subscripts ($f$) and ($i$) refer to final and initial quantities).

For both coordinates, $(\partial\mu/\partial S)$ (cf. Column 2 of Table 5) is seen to be smaller in magnitude when the BH$_3$CO $\pi$ interaction is permitted. It is uncertain, at this early stage in the history of using zero differential overlap methods to analyze $\partial\mu/\partial S$, what conditions lead to useful values for the initial charge, charge relaxation, and hybridization components of $\partial\mu/\partial S$. For the sake of completeness these quantities are given in columns 3–5 of Table 5. Clearly the hybridization contribution to $\partial\mu/\partial S$ is dominated by the combined charge-displacement, charge-relaxation terms (note, however, that the hybridization term opposes the charge terms and is of appreciable magnitude for the bending coordinate of the normal

Table 5. Dipole moment derivatives

| Coordinate | $\partial\mu/\partial S$ | $\partial\mu(sp)/\partial S$ | $\partial\mu(q \cdot \varDelta r)/\partial S$ | $\partial\mu(\varDelta q \cdot r)/\partial S$ |
|---|---|---|---|---|
| $a_1$ str (norm.) | 0.42 | $-0.05$ | 0.01 | 0.47 |
| (nohyper) | 0.88 | $-0.02$ | 0.25 | 0.65 |
| $\delta$ | $-0.45$ | $-0.03$ | $-0.24$ | $-0.18$ |
| $a_1$ bend (norm.) | $-0.16$ | 0.28 | $-0.02$ | $-0.42$ |
| (nohyper) | $-0.95$ | 0.06 | $-0.70$ | $-0.30$ |
| $\delta$ | 0.79 | 0.22 | 0.68 | $-0.11$ |

calculation). For the normal calculations of both coordinates the charge relaxation term dominates the dipole derivative. However, the effect of hyperconjugation to decrease the dipole derivative arises primarily through the initial charges term, with substantial effects from the other two terms. Unfortunately, breakdown of these contributions to separate $\sigma$ and $\pi$ orbital effects is not meaningful because the separate results depend on how each nuclear charge is divided between $\sigma$ and $\pi$ electrons.

Before closing on this topic we should note that the absorption bands actually observed fn an infrared experiment correspond to normal modes, any one of which may involve motion of atoms other than these used in defining the symmetry coordinate. This cautions that the magnitude of the intensity of an infrared band (say the $a_1$ bending mode) may be unreliable as a measure of hyperconjugation so that reasonably firm conclusions would be justified only after determination of the $(\partial\mu/\partial S)$. Another potential complication arises for the $a_1$ $BH_3$ stretching mode which is often observed to be in Fermi resonance with the overtone of the $a_1$ bending coordinate [6]. Consequently, while intensities of the $a_1$ $BH_3$ modes seem to offer a quite sensitive probe of hyperconjugation, the use of those intensities, in fact, is not clear cut. Particularly bothersome is the difficulty of not being able to isolate $\sigma$ and $\pi$ contributions and this is compounded by the necessity of *fully* analyzing the normal modes of each $BH_3$ adduct.

## 4. Summary

The word hyperconjugation is most appropriate to apply to $\pi$ type interactions of the $BH_3$ group; many molecular properties of $BH_3$ adducts are simply not sufficiently sensitive to hyperconjugation to warrant their use as probes of the $\pi$ orbital conjugation. These studies have identified $^2J_{HH}$ couplings and the $^{11}B$ quadrupole coupling constants as two potentially useful probes of the binding of $BH_3$ to donors. Finally, analysis of the interaction between $BH_3$ and $CO$ suggests that interpretation of molecular properties of such adducts may depend not only on the inherent (and loosely defined) $\sigma$ donor and $\pi$ acceptor properties of bases but additionally on the effectiveness of amplification of the $\sigma$ donor character by $\pi$ acceptor ability.

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