gave a ^1H signal at τ -0.25. Potassium fluorosulfonate (0.01 g) was added, most of the salt settling to the bottom of the tube. Redetermination of the ^1H nmr spectrum showed that the fluorosulfonic acid signal had broadened and shifted to τ -0.66.

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Orbital Following and Hyperconjugation in Borane Adducts

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It is the purpose of this article to comment on the hybrid orbital force field (HOFF) model of Mills[1] as it applies to the compliance constants[2] of a series of borane adducts. Compliance constants are the elements of the inverse force constant matrix for a molecule and the HOFF model has been developed for the purpose of estimating the signs and magnitudes of interaction force constants. The HOFF model envisions hybrid orbital following of nuclear motions as the source of interaction force constants which are involved in the definition of compliance matrix elements. The latter are in turn related to interaction coordinates.

Jones and Ryan have shown[3] how the interaction coordinates may be obtained from the elements of $\mathbf{C} = \mathbf{F}^{-1}$. $(S_3)_2$, for example, is defined as $(\mathrm{d}S_3/\mathrm{d}S_2)_{v=\min}$ and has the value C_{32}/C_{22}. According to Mills' formulation[1] in terms of hybrid orbital following, $\mathrm{d}S_3/\mathrm{d}S_2 = (\mathrm{d}S_3/\mathrm{d}\lambda_x)(\mathrm{d}\lambda_x/\mathrm{d}S_2)$. λ_x is the hybridization parameter in $\phi_\mathrm{h} = (1 + \lambda_x^2)^{-1/2}(\phi_\mathrm{s} + \lambda_x\phi_\mathrm{p})$ for the B–X bond. In the cases which are to be discussed, S_3 refers to the B–X stretching coordinate and S_2 refers to the BH_3 bending coordinate, both of A_1 symmetry.

Before discussing the $(S_3)_2$ interaction coordinates for the BH_3X adducts in detail, it is of interest to examine the compliance constant for S_3. In general, if there are interaction force constants between S_3 and the other A_1 coordinates $C_{33} \neq 1/F_{33}$. The difference is due to relaxational effects within the BH_3 fragment which arise when the molecule is subjected to a force along S_3. C_{33} (units are Å/mdyn), then, measures the response of S_3 to that force while allowing the other coordinates to achieve their minimum energy configuration.

Table I gives the values of C_{33} for a series of adducts which have recently been subjected to the HOFF treatment of the normal modes.[4] Compare, with regard to the comments in the last paragraph, the closeness of F_{33} for X = PF_3 and NMe_3 but the greater difference in C_{33}.

TABLE I

COMPLIANCE AND FORCE CONSTANTS FOR S_3 OF BH_3X^-

	C_{33}[a]	F_{33}[b]	$\Delta = C_{33} - 1/F_{33}$
F^-	0.204	5.68	+0.028 (+14%)
CN^-	0.256	4.56	+0.037 (+14%)
NC^-	0.306	3.36	+0.008 (+3%)
CO	0.383	2.78	+0.023 (+6%)
NH_3[c]	0.397	2.90	+0.053 (+13%)
PF_3	0.444	2.39	+0.026 (+6%)
NMe_3[c]	0.494	2.36	+0.070 (+14%)

[a] Units are Å/mdyn. [b] Units are mdyn/Å. [c] See R. C. Taylor, *Advan. Chem. Ser.*, **No. 42**, 67 (1964).

Comparison of the B–X displacements per unit force with those calculated from F_{33}^{-1} shows that reorganization at BH_3 facilitates B–X displacement by +14% for all but CO and PF_5 (and NC^-). The enhancement is thus small but detectable. The low values for CO and PF_3 may be attributed to hyperconjugation in those adducts, hyperconjugation playing a resistive role to B–X elongation. The effect is small[5] however (~8%) and of minor importance to the adduct bonds and probably the chemistries of BH_3CO and BH_3PF_3.

The low value of $C_{33} - F_{33}^{-1}$ for BH_3NC^- would imply a singularly unresponsive BH_3 fragment in that adduct. This value is subject to some question, however, since there are several possibilities for small errors in the force field of this molecule, not the least of which is the difficulty in assigning band positions with high accuracy.[4]

Another feature of the compliance matrix which is interesting to examine is the ratio C_{32}/C_{22} which gives the interaction coordinate $(S_3)_2 = \mathrm{d}S_3/\mathrm{d}S_2$. According to the HOFF model of Mills, $(S_3)_2$ may be calculated from the set of orthogonality conditions for the boron hybrids ($\lambda_i\lambda_j \cos \alpha_{ij} + 1 = 0$) and the definition of $S_2 = c[\alpha_1 + \alpha_2 + \alpha_3 - b(\beta_1 + \beta_2 + \beta_3)]$. The quantities c and b are chosen to ensure orthonormality of S_2 and the angle redundancy coordinate, the latter being null to first order. With

$$\frac{\mathrm{d}S_3}{\mathrm{d}S_2} = \frac{\mathrm{d}S_3}{\mathrm{d}\lambda_x}\frac{\mathrm{d}\lambda_x}{\mathrm{d}S_2}$$

we find for $\mathrm{d}\lambda_x/\mathrm{d}S_2$ from S_2 and the orthogonality equations

$$\frac{\mathrm{d}\lambda_x}{\mathrm{d}S_2} = \lambda_x K$$

where

$$K = -\frac{1}{6}\sqrt{3 + \frac{\cos^2 \alpha/2}{\cos^2 \beta}}\left[\tan \beta - \frac{\sqrt{3}}{2}\frac{\cos \beta \tan \alpha}{\cos \alpha/2}\right] \mathrm{rad}^{-1}$$

Here $\alpha = \angle$HBH and $\beta = \angle$HBX. To evaluate $\mathrm{d}S_3/\mathrm{d}\lambda_x$ we may try $\mathrm{d}S_3/\mathrm{d}\lambda_x = \mathrm{d}\bar{\phi}_h/\mathrm{d}\lambda_x$, where

$$\phi_h = \frac{1}{1 + \lambda_x^2}[\phi_\mathrm{s} + \lambda_x\phi_\mathrm{p}]$$

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(1) I. M. Mills, *Spectrochim. Acta*, **19**, 1585 (1963).

(2) J. C. Decius, *J. Chem. Phys.*, **38**, 241 (1963).

(3) L. H. Jones and R. R. Ryan, *ibid.*, **52**, 2003 (1970).

(4) J. R. Berschied and K. F. Purcell, in press.

(5) For the series CH_3X, we find (unpublished) enhancement of C_{33} by 11% for X = F, Cl, Br, I. With X = CN, CCH, CCCl, CCBr, the enhancement is only 5%, while it is 8% for X = NC. Thus, as far as electron rearrangement following nuclear displacement is concerned, hyperconjugation is hardly more important to BH_3 than it is to CH_3. For the force fields of CH_3X, see J. Aldous and I. M. Mills, *Spectrochim. Acta*, **18**, 1073 (1962), and J. L. Duncan, *ibid.*, **20**, 1197 (1964).

is the boron hybrid to X and

$$\bar{\phi}_h \left[= \frac{1}{1 + \lambda_x{}^2} [\bar{\phi}_s + \lambda_x{}^2 \bar{\phi}_p] \right]$$

signifies the average radial distance of ϕ_h. Using Slater functions for ϕ_s and ϕ_p $\{\phi = [(2\zeta)^{5/2}/(4!)^{1/2}]re^{-\zeta r}\}$, we find

$$\frac{d\bar{\phi}_h}{d\lambda_x} = 2[\bar{\phi}_p - \bar{\phi}_s] \frac{\lambda_x}{(1 + \lambda_x{}^2)^2}$$

Thus

$$\frac{dS_3}{dS_2} \cong (2\Delta R)K \frac{\lambda_x{}^2}{(1 + \lambda_x{}^2)^2} = 2(\Delta R)K(f_s f_p)$$

where f_s and f_p are the fractional s and p characters of the B hybrid to X. By including the variation in K with λ_x, we compute the curve in Figure 1 for $(S_3)_2 = f(f_s)$. This curve is developed by treating ΔR as a parameter, a value of 0.2 for which yields $dS_3/d\lambda_x = 0.06$ Å for sp^2 boron and 0.04 Å for sp^3 boron, values which are in accord with chemical intuition.[6] When the experimental values of $(S_3)_2$ are placed on this curve, qualitatively reasonable results are obtained for the boron hybridization. With CN$^-$ as the donor the boron is seen to take on ~sp^3 character, a value consistent with the reported value[7] of $J_{^{11}BH}$ for BH$_3$CN$^-$. The isoelectronic BH$_3$CO is found to involve ~16% B s character in the hybrid to CO. (CNDO/2 calculations[4] give 26% and 19% s character for these hybrids, respectively.) Similarly F$^-$ and PF$_3$ are found to involve <25% B s characters in the B–X bonds, as expected. An especially low value for BH$_3$NC$^-$ is to be noted. As mentioned above, there may be some error in the force field for this molecule which results in the low value. Values for the NH$_3$ and NMe$_3$ adducts[8] are included in Figure 1 but must be treated as tentative. Those values were not computed according to the same constraints as were those of the other adducts[4] and all force constants for these two adducts were reported in units of mdyn/Å with no indication of the value of r used in the unit conversion for bending coordinate constants. The per cents of s character for these adducts are not unreasonable, however.

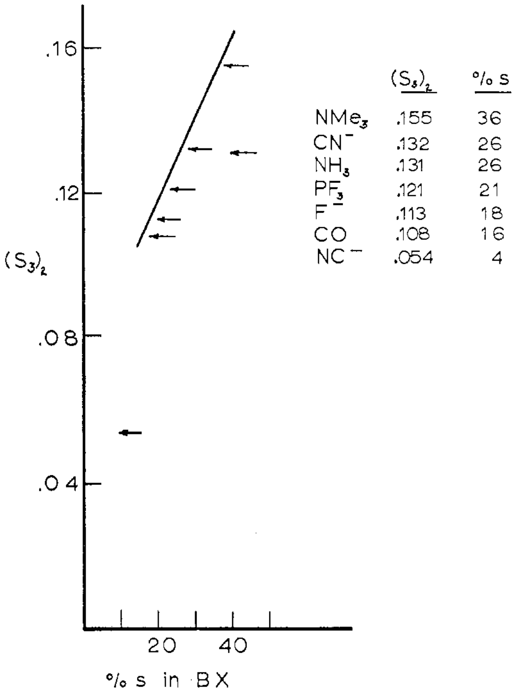

Figure 1.—Adduct bond stretch with respect to BH$_3$ bend interaction coordinate as a function of boron per cent of s character in the adduct bond. The solid line is the theoretical curve and experimental values of $(S_3)_2$ are indicated with arrows (see insert).

The effect of BH$_3$ hyperconjugation is expected to be barely discernible in Figure 1. While B–X back-donation would serve to reduce $(S_3)_2$, no drastic reduction is found for BH$_3$CO and BH$_3$PF$_3$. In fact, the per cent of s character for BH$_3$CO estimated from Figure 1 is in good agreement with that deduced from the CNDO/2 description of the B–C σ bond.

In conclusion, we find the HOFF model to be applicable to these BH$_3$X adducts with semiquantitative results. This approach to orbital following of nuclear displacement also indicates that BH$_3$ hyperconjugation is observable with X = CO or PF$_3$ but that the B–X π-bond interaction is much less significant to BH$_3$ electron reorganization during nuclear displacement than is the σ-bond interaction.

Acknowledgment.—We wish to thank the National Science Foundation for support of this research through Grant GP-28924.

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[6] A rough experimental value for carbon is 0.03 Å.[1]

[7] J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 624 (1970).

[8] R. C. Taylor, *Advan. Chem. Ser.*, **No. 42**, 67 (1964).

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2-Substituted 1,3,2-Benzodioxaphosphole Derivatives of Tungsten Hexacarbonyl

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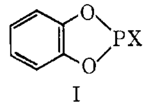
In connection with our current interest in phosphorus–transition metal chemistry, we wish to report some 2-substituted 1,3,2-benzodioxaphosphole (I) derivatives of tungsten hexacarbonyl of the type C$_6$H$_4$O$_2$P(X)W(CO)$_5$, where X = Cl or N(C$_2$H$_5$)$_2$.



I

The new compounds were obtained by the reactions of the appropriate ligands, I, with the tetrahydrofuran complex of tungsten pentacarbonyl, prepared *in situ* by the irradiation of a solution of tungsten hexacarbonyl in tetrahydrofuran.[1] Related metal complexes of I with X = F have been reported by Schmutzler.[2] The chlorophosphole[3] was prepared by the reaction of phosphorus trichloride with catechol and converted

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[1] W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).

[2] R. Schmutzler, *Ber.*, **96**, 2435 (1963).

[3] P. C. Crofts, J. H. H. Markes, and H. N. Rydon, *J. Chem. Soc.*, 4250 (1958).