packed with Porapak Q. Quantitation was performed by means of a Vidar 6300 digital integrator and standard calibration curves. Raman spectrum of solid at −80 °C: 3557 vw, 3469 vw, 1169 m, 1009 w, 891 vw, 848 vw, 802 w, 650 vw, 615 m, 472 w, 422 s, 382 m, 337 w, 285 m, 269 m.

Preparation of *erythro*- and *threo*-2-(2′,2′,2′-Trichloro-1′-hydroxyethyl)cyclohexanone.[25,14] To a solution of 33.69 g (0.202 mol) of 1-morpholino-1-cyclohexene[26] in 100 ml of dry chloroform contained in a 300-ml round-bottomed flask equipped with a stirring bar, addition funnel, and nitrogen inlet tube was added a solution of 31.45 g (0.213 mol) of chloral in 50 ml of dry chloroform over a 1-h interval. After the addition the solution was permitted to stir in a dry nitrogen atmosphere at room temperature for 2 h. At the end of the stirring period 75 ml of an acetic acid-sodium acetate buffer was added; the resulting mixture was refluxed for 2 h.

At the end of the reflux period the aqueous layer was separated from the organic layer and washed with 25 ml of $HCCl_3$ and the organic layers were combined, washed with 75 ml of saturated sodium bicarbonate, 75 ml of saturated sodium chloride, and 75 ml of water and dried over anhydrous $MgSO_4$. After filtration and removal of the chloroform by rotary evaporation, 31.2 g of an oil was obtained that appeared to be about a 50:50 mixture of both isomers by ^1H NMR. The erythro and threo isomers were obtained in pure form by chromatography on silicic acid (Mallinckrodt, Silicic Acid A. R. 100 mesh, Chromatography Grade) using 20% (by volume) petroleum ether in benzene as eluent. The melting points, ir, and ^1H NMR spectra of the two isomers agreed with those of Kiehlman and Loo.[14]

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Borine Carbonyl. Bonding and Properties in the Single-Determinant Approximation

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Abstract: Using the Hartree–Fock–Roothaan approximation, we investigate the $^1A_1$ ground electronic state of borine carbonyl with two Slater and two contracted Gaussian basis sets. The total energies range from −138.6832 au for a minimal (2s1p/1s) Slater basis to −139.1723 au for a near-Hartree-Fock (9s5p1d/2s1p)/[5s3p1d/2s1p] Gaussian basis. The Hartree-Fock limit energy, which is estimated to be −139.210 ± 0.004 au, is employed to extract the molecular extra correlation energy of −0.21 ± 0.01 au. Reaction energies relative to the decomposition of BH_3CO are also examined in terms of Hartree-Fock and correlation contributions. A variety of one-electron properties are computed and compared with available measurements. Hybridization of the orbitals at boron and other local features of the bonding are discerned from electron density maps.

I. Introduction

Borine carbonyl is an example of what Mulliken[2] has termed a "two-way donor-acceptor complex", namely a loose confederation in which the BH_3 and CO fragments function more or less as both electron donors and acceptors. Although the preparation,[3a] chemical properties,[3a] and molecular structure[3b-7] of this complex were first reported in 1937, only three ab initio theoretical studies[8-10] have appeared on its ground $^1A_1$ electronic state and these were carried out without polarization functions in the basis set. Apart from these studies, the charge distribution has been interpreted semiquantitatively in terms of resonances between valence-bond structures[2,3b,5] and with semiempirical molecular orbital (MO) theory.[11,12] It therefore appears

Table I. Experimental Equilibrium Geometry of BH_3CO (au)[a]

Atom	X	Y	Z
B	0.0	0.0	0.0
C	0.0	0.0	2.910 218
O	0.0	0.0	5.047 527
H1	2.183 440	0.0	−0.569 003
H2	−1.091 719	1.890 915	−0.569 003
H3	−1.091 719	−1.890 915	−0.569 003

[a] Reference 5 (1 au = 0.529 17 Å).

that a modern theoretical analysis of the bonding in this rather unusual molecule would be very worthwhile, especially in view of the significant advances in quantum chemistry during the period since BH_3CO was first characterized.

In this paper, we examine BH_3CO with two Slater- and two Gaussian-type basis sets in the Hartree-Fock approximation. The latter contain polarization functions and approach the Hartree–Fock-limit energy within an estimated 0.04 au for the X^1A_1 state. The corresponding self-consistent field (SCF) wave functions are used for population analyses and for the determination of numerous one-electron properties which are compared with the available experimental data. The minimal basis set canonical MO's are transformed into localized inner-shell, bond-, and lone-pair orbitals which are plotted and analyzed by the tenets of valence theory. Reaction energies for the decomposition of BH_3CO are also studied.

II. Calculations

The geometry adopted for our calculations is given in Table I where we list the Cartesian coordinates for the six nuclei. This skeleton corresponds to the equilibrium structure derived by Gordy, Ring, and Burg[5] from the microwave spectrum (CO, BC, and BH bond lengths of 1.131, 1.540, and 1.194 Å; HBH angle of 113°52′). Note that the molecule has C_{3v} symmetry and that the heavy atoms are aligned axially in a B–C–O sequence.

In ab initio studies, it is instructive to begin with a minimal basis set and then gradually add basis functions to allow for core and valence polarizations of the electron distribution. Our minimal Slater (STO) basis set, (2s1p/1s) in a commonly used notation, consists of 18 functions with the orbital exponents given in Table IIA. The exponents were taken from optimized values for BH_3[13] and CO_2.[14] The CO_2 molecule was used instead of CO because borine carbonyl resembles CO_2 if the BH_3 group is regarded as a perturbed oxygen atom. To improve this (2s1p/1s) set, the p orbitals on each of the heavy atoms were split into two Sla-

Table II. Basis Sets for BH_3CO

Atom	Type	Exponent	Coefficient
	A. Minimal Slater (2s1p/1s) Set		
B	1s	4.68	
	2s	1.42	
	2p	1.47	
C	1s	5.6726	
	2s	1.6082	
	2p	1.5680_5	
O	1s	7.6580	
	2s	2.2461	
	2p	2.2262_5	
H	1s	1.19	
	B. Augmented Slater (2s2p/1s) Set		
B	1s	4.68	
	2s	1.42	
	2p	1.0036_6	
	2p′	2.2085_5	
C	1s	5.6726	
	2s	1.6082	
	2p	1.2557_2	
	2p′	2.2762_5	
O	1s	7.6580	
	2s	2.2461	
	2p	1.6537_2	
	2p′	3.6812_7	
H	1s	1.19	
	C. Double-ζ Gaussian (9s5p/4s)/[4s3p/2s] Set		
B	s	2788.41	0.002 122
		419.039	0.016 171
		96.4683	0.078 356
		28.0694	0.263 250
		9.3760	0.596 729
		1.3057	0.230 397
	s′	3.4062	1.000 000
	s″	0.3245	1.000 000
	s‴	0.1022	1.000 000
	p	11.3413	0.038 707
		2.4360	0.237 448
		0.6836	0.824 446
	p′	0.2134	1.000 000
	p″	0.0710	1.000 000
C	s	4232.61	0.002 029
		634.882	0.015 535
		146.097	0.075 411
		42.4974	0.257 121
		14.1892	0.596 555
		1.9666	0.242 517
	s′	5.1477	1.000 000
	s″	0.4962	1.000 000
	s‴	0.1533	1.000 000
	p	18.1557	0.039 196
		3.9864	0.244 144
		1.1429	0.816 775
	p′	0.3549	1.000 000
	p″	0.1146	1.000 000
O	s	7816.54	0.002 031
		1175.82	0.015 436
		273.188	0.073 771
		81.1696	0.247 606
		27.1836	0.611 832
		3.4136	0.241 205
	s′	9.5322	1.000 000
	s″	0.9398	1.000 000
	s‴	0.2846	1.000 000
	p	35.1832	0.040 023
		7.9040	0.253 849
		2.3051	0.806 842
	p′	0.7171	1.000 000
	p″	0.2137	1.000 000
H	s	19.2406	0.032 828
		2.8992	0.231 209
		0.6534	0.817 240
	s′	0.1776	1.000 000
	D. Polarization Functions for the Gaussian (9s5p1d/4s1p)/[4s3p1d/2s1p] Set		
B	d	0.85	1.000 000
C	d	1.00	1.000 000
O	d	1.00	1.000 000
H	p	1.10	1.000 000

Table III. Energies[a] for the Ground Electronic State of BH_3CO in the Single Determinant Approximation (au)

	Slater		Gaussian	
	(2s1p/1s)	(2s2p/1s)	(9s5p/4s) [4s3p/2s]	(9s5p1d/4s1p) [4s3p1d/2s1p]
E	−138.683 23	−138.935 89	−139.089 62	−139.172 28
$\epsilon(1a_1)$	−20.898 6	−20.768 4	−20.738 2	−20.718 1
$\epsilon(2a_1)$	−11.568 5	−11.528 6	−11.465 8	−11.441 2
$\epsilon(3a_1)$	−7.512 5	−7.588 4	−7.560 6	−7.551 6
$\epsilon(4a_1)$	−1.595 8	−1.634 3	−1.608 9	−1.571 6
$\epsilon(5a_1)$	−0.883 2	−0.929 9	−0.905 5	−0.903 2
$\epsilon(6a_1)$	−0.753 7	−0.814 4	−0.797 8	−0.800 5
$\epsilon(1e)$	−0.686 3	−0.734 0	−0.702 2	−0.693 9
$\epsilon(7a_1)$	−0.530 9	−0.592 6	−0.565 6	−0.563 9
$\epsilon(2e)$	−0.439 9	−0.494 5	−0.472 5	−0.472 0

[a] The symbols E and ϵ refer to total and orbital energies, respectively.

Table IV. Reaction Energies Involving BH_3CO[a]

Energy quantity	(2s1p/1s)	(9s5p/4s) [4s3p/2s]	(9s5p1d/4s1p) [4s3p1d/2s1p]	Hartree-Fock[b]	Electron correlation[c]	Exptl[d]
$E(BH_3\text{-}CO)$	−138.6832	−139.0896	−139.1723	−139.210	−0.744	−139.954
$E(BH_3)$[e]	−26.3509	−26.3799	−26.3959	−26.403	−0.195	−26.598
$E(CO)$[f]	−112.3260	−112.6969	−112.7662	−112.796	−0.520	−113.316
$E(B_2H_6)$[g]	−52.7152	−52.7778	−52.8211	−52.835	−0.429	−53.264
$\Delta E(1)$[h]	4.0	8.1	6.4	6.4	18.7	25.1
$\Delta E(2)$[i]	−0.5	4.8	−5.5	−5.5	11.9	6.4
$\Delta E(3)$[j]	8.4	11.4	18.3	18.3	24.4	42.7

[a] All total energies (E) and reaction energies (ΔE) are given, respectively, in atomic units and kcal/mol (1 au = 627.5 kcal/mol). [b] Estimated by the rule proposed in ref 31. [c] Obtained as the difference of the Hartree-Fock and experimental energies. [d] The total energies E are obtained by a suitable combination of data in ref 23 and 31; the ΔE's are derived from these data by simple subtraction. All values refer to the bottom of the potential well and exclude relativistic contributions. Kinetic and mass spectroscopic measurements of ΔH_f for these reactions often differ markedly: for example, ΔH_f for B_2H_6 in reaction 3 range from −25 to 38 kcal/mol for kinetic measurements[23] and from −39 to −59 kcal/mol for mass spectroscopic measurements.[24] [e] $R(B\text{-}H) = 1.196$ Å, $\angle HBH = 120°$. [f] $R(C\text{-}O) = 1.1281$ Å. [g] $R(B\text{-}B) = 1.775$ Å, $R(B\text{-}H_t) = 1.196$ Å, $R(B\text{-}H_b) = 1.339$ Å, $\angle H_tBH_t = 120.2°$. [h] Reaction 1 of text. [i] Reaction 2 of text. [j] Reaction 3 of text.

ter functions with exponents taken from double-ζ atomic sets of Clementi.[15] The resulting (2s2p/1s) Slater basis is defined explicitly in Table IIB. A wave function of full double-ζ quality also requires a splitting of the s exponents, which we accomplish with the (9s5p/4s)/[4s3p/2s] contracted Gaussian basis (GTO) introduced by Dunning.[16a] The exponents and contraction coefficients are listed in Table IIC. To approach the Hartree-Fock limit, it is necessary to include polarization functions[16b] in the basis set, that is p functions on H and d functions on B, C, and O. Examination of calculations on other molecules (e.g., H_2O,[16b] N_2,[16b] CO,[17] and CH_4[18]) suggests that the set of exponents in Table IID are reasonably chosen for BH_3CO when added to the (9s5p/4s)/[4s3p/2s] GTO set to form a (9s5p1d/4s1p)/[4s3p1d/2s1p] set.

Single-determinant, self-consistent-field (SCF) calculations of the Roothaan[19] type were performed with these four basis sets at the equilibrium BH_3CO geometry. For the STO and GTO sets, respectively, we employed Steven's POLYCAL system of programs[20] and the POLYATOM system[21] as modified according to the algorithm of Pitzer.[22] The total and orbital energies corresponding to each of the four wave functions are given in Table III.

To examine energy changes for certain reactions involving BH_3CO, we have also performed computations on BH_3, CO, and B_2H_6. These are listed for the minimal STO and the Gaussian bases in Table IV where correlation contributions and experimental energies[23] are also given. Orbital energies for our largest basis set are shown in Table V. The specific reactions that we consider are

$$BH_3CO = BH_3 + CO \quad (1)$$

$$2BH_3CO = B_2H_6 + 2CO \quad (2)$$

and

$$B_2H_6 = 2BH_3 \quad (3)$$

Inspection shows that only two of these reactions are independent, but it is useful to tabulate all three of them to determine consistency with experimental data.[23,24] Population analyses for each of the four BH_3CO wave functions are given in Table VI and a comparison of population analyses for the molecules involved in reaction 1 is presented in Table VII.

A series of one-electron properties has also been computed with each of our four wave functions. These are reported in Table VIII and include the molecular dipole moment (μ), the nuclear-electron potential ($\langle 1/r \rangle$), electric field (**E**), and electric-field gradients (**q**) at selected nuclei, and the molecular quadrupole moment at the center of mass (θ).

We have transformed minimal STO-basis set MO's so as to maximize the intra-orbital repulsion energies using a computer program by Liang,[25] which accomplishes this by the method[26] of principal ascents. The result is a description of the electron distribution that resembles the traditional concepts of "pair bonds", "lone pairs", and "inner shells". Table IX contains the atomic orbital coefficients for these "localized" MO's (LMO's). An analysis of the hybridiza-

Table V. Molecular Orbital Energies for the BH_3CO Complex and Its Component Fragments Relative to a (9s5p1d/4s1p)/[4s3p1d/2s1p] Basis Set (au)[a]

BH_3CO	BH_3[b]	CO[b]	BH_3[c]	CO[c]
0.1745 ($8a_1$)	0.0405 ($3a_1$)		0.0555 ($1a_2''$)	
0.0995 (3e)		0.1337 (2π)		0.1348 (2π)
−0.4720 (2e)	−0.4876 (1e)		−0.4974 (1e′)	
−0.5639 ($7a_1$)		−0.5550 (5σ)		−0.5547 (5σ)
−0.6939 (1e)		−0.6373 (1π)		−0.6386 (1π)
−0.8005 ($6a_1$)	−0.7069 ($2a_1$)		−0.7036 ($2a_1'$)	
−0.9032 ($5a_1$)		−0.8023 (4σ)		−0.8026 (4σ)
−1.5716 ($4a_1$)		−1.5221 (3σ)		−1.5241 (3σ)
−7.5516 ($3a_1$)	−7.6142 ($1a_1$)		−7.6122 ($1a_1'$)	
−11.4412 ($2a_1$)		−11.3631 (2σ)		−11.3618 (2σ)
−20.7181 ($1a_1$)		−20.6665 (1σ)		−20.6667 (1σ)

[a] The symmetry designations with respect to the C_{3v}, $C_{\infty v}$, or D_{3h} point groups are given in parentheses. [b] Geometry corresponding to that in BH_3CO (see Table I). $E_{BH_3} = -26.3740$ au, $E_{CO} = -112.7658$ au. [c] Geometry corresponding to the isolated molecules at equilibrium (see Table IV).

Table VI. Population Analysis for BH_3CO Relative to Four Basis Sets[a]

	STO		GTO	
Population	(2s1p/1s)	(2s2p/1s)	(9s5p/4s) [4s3p/2s]	(9s5p1d/4s1p) [4s3p1d/2s1p]
Gross atomic charge				
B	0.020	−0.196	−0.244	−0.116
H	−0.054	0.031	0.034	−0.020
C	0.251	0.546	0.428	0.485
O	−0.108	−0.441	−0.286	−0.308
Overlap				
C, O	1.144	1.175	1.270	1.374
B, H	0.791	0.824	0.823	0.833
B, C	0.378	0.281	0.103	0.317
H, C	−0.045	−0.060	−0.048	−0.041
H, H	−0.020	−0.008	−0.030	−0.028
B, O	−0.001	−0.121	−0.002	−0.022
H, O	−0.000	−0.001	−0.003	−0.002

[a] Defined according to R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

Table VII. Population Analysis of the BH_3CO Complex and Its Component Fragments Relative to a (9s5p1d/4s1p)/[4s3p1d/2s1p] Basis Set[a]

Population[b]	BH_3CO	BH_3[c]	CO[c]	BH_3[d]	CO[d]
Gross					
B	3.356	3.035		3.040	
	1.760	1.808		1.776	
H	0.341	0.322		0.321	
	0.679	0.731		0.741	
C	4.359		4.719		4.719
	1.156		0.939		0.940
O	5.261		5.282		5.281
	3.047		3.061		3.061
Overlap					
C, O	0.601		0.304		0.304
	0.773		0.806		0.808
B, H	0.331	0.287		0.289	
	0.502	0.537		0.541	
B, C	0.184				
	0.133				
H, C	−0.068				
	0.027				
H, H	0.042	0.035		0.032	
	−0.070	−0.077		−0.069	
B, O	−0.008				
	−0.014				
H, O	0.001				
	−0.003				

[a] Defined according to R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955). [b] Contributions from the $a_1(\sigma)$- and $e(\pi)$-type MO's are given for each atom and atom pair, respectively. [c] Geometry corresponding to that in BH_3CO (see Table I). [d] Geometry corresponding to the isolated molecules at equilibrium (see Table IV).

tion of the boron atom in BH_3CO is extracted from these data and is presented in Table X. A pictorial display of the LMO's can be seen from the series of electron density maps in Figures 1-5, which were prepared using a computer program written by Palke and Hegstrom.[27] Since the transformation between the canonical MO and LMO representations is unitary, integration over these LMO maps leads, with the appropriate operator as the weighting factor, to the same total property values as those given in column I of Table VIII. The contributions to the dipole moment of BH_3CO from each of the LMO's relative to the boron and carbon atoms as origins are listed in Table XI.

III. Discussion

Enlargements of the basis set bring about significant improvements in the total energy of the borine carbonyl molecule. As Table III shows, the energy decreases by 0.48905 au (or about 13.3 eV) between the minimal-Slater and Gaussian-plus-polarization basis sets. The best published ab initio calculation for BH_3CO to date is that of Snyder and Basch.[9b] Using (10s5p/4s)/[4s2p/2s] basis but a somewhat different geometry from that used here, they obtained an energy of −139.0670 au which is higher than our best value by 0.1053 au. It is instructive to compare how similar changes of basis affect the total energy of some molecule for which the Hartree-Fock limit has been better established.

Consider the water molecule for which an optimized Slater basis, (2s1p/1s), yields a total energy[28] of −75.7033 au, while a Gaussian-plus-polarization basis, (9s5p1d/4s1p)/[4s3p1d/2s1p], gives[16] −76.0467 au, for an energy lowering of 0.3434 au. The Hartree-Fock-limit energy of water is estimated to be −76.067 ± 0.001 au based on recent calculations.[29,30] Thus, the Gaussian-plus-polarization basis recovers about 94% of the Hartree-Fock minus minimal-basis energy difference. If this same percentage obtains for BH_3CO, we would estimate the Hartree-Fock limit to be

Table VIII. Selected Properties of the Ground Electronic State of BH_3CO (au)[a]

	Slater		Gaussian	
Property	(2s1p/1s)	(2s2p/1s)	(9s5p/4s) [4s3p/2s]	(9s5p1d/4s1p) [4s3p1d/2s1p]
$\mu_z(C^+B^-)$	1.0633	0.5549	0.6352	0.7139
$\langle E_z \rangle_B$	0.0550	0.0434	0.0325	0.0214
$\langle E_z \rangle_C$	0.1688	0.1177	0.1107	0.0124
$\langle E_z \rangle_O$	−0.4103	−0.3550	−0.2446	−0.0682
$\langle E_x \rangle_{H1}$	−0.0334	−0.0869	−0.0595	−0.0079
$\langle E_z \rangle_{H1}$	0.0292	0.0453	0.0299	0.0068
$\langle E_x \rangle_{H2}$	0.0167	0.0434	0.0298	0.0040
$\langle E_y \rangle_{H2}$	−0.0290	−0.0752	−0.0516	−0.0069
$\langle \mathcal{F}_z \rangle$	1.9070	1.7809	1.0404	0.3438
$\langle q_{xx} \rangle_B$	−0.1625	−0.1245	−0.1130	−0.1108
$\langle q_{zz} \rangle_B$	0.3251	0.2490	0.2260	0.2217
$\langle q_{xx} \rangle_O$	−0.0407	0.1981	0.1052	0.1733
$\langle q_{zz} \rangle_O$	0.0813	−0.3963	−0.2103	−0.3467
$\langle q_{x'x'} \rangle_{H1}$	−0.1009	−0.1127	−0.1036	−0.0945
$\langle q_{y'y'} \rangle_{H1}$	−0.1218	−0.1400	−0.1315	−0.1187
$\langle q_{z'z'} \rangle_{H1}$	0.2227	0.2527	0.2351	0.2132
φ (rot. of xz plane), deg	16.48	16.90	16.14	15.14
$\langle \theta_{xx} \rangle_{CM}$	2.0522	2.2038	2.3384	2.0129
$\langle \theta_{zz} \rangle_{CM}$	−4.1044	−4.4075	−4.6768	−4.0258
$\langle 1/r \rangle_B$	16.4543	16.3870	16.4436	16.4506
$\langle 1/r \rangle_C$	20.5639	20.6250	20.7289	20.7480
$\langle 1/r \rangle_O$	26.2442	26.4130	26.4705	26.4849

[a] For definitions, see D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968).

−139.20 au based on the results in Table III. An even simpler device[31] that we have found useful in approximating this limit is to multiply the (9s5p1d/4s1p)/[4s3p1d/2s1p] energy by the ratio of the Hartree-Fock-limit energy of water to its energy calculated with this same basis set (1.00027 ± 0.00003), yielding $E(\mathrm{HF}) = -139.210 \pm 0.004$ au in the case of BH_3CO.

If we take this value of $E_{BH_3CO}(\mathrm{HF})$ as the correct one, we can extract the molecular extra correlation energy $\Delta E_{BH_3CO}(\mathrm{corr})$ from the definition[32]

$$\Delta E_{BH_3CO}(\mathrm{corr}) = E_{BH_3CO}(\mathrm{corr}) - \sum_k E_k(\mathrm{corr}) \quad (4)$$

which can be written as

$$\Delta E_{BH_3CO}(\mathrm{corr}) = \sum_k E_k(\mathrm{HF}) - E_{BH_3CO}(\mathrm{HF}) - D_e \quad (5)$$

where k indexes the atoms and D_e is the dissociation energy measured from the bottom of the potential well. We assume here that the difference between the atomic and molecular relativistic energies is negligible. Given the atomic Hartree-Fock energies[33] which sum to −138.527 au and the value[6,23] of $D_e = 0.90 \pm 0.01$ au, we find from eq 5 $\Delta E_{BH_3CO}(\mathrm{corr}) = -0.21 \pm 0.01$ au. Now using eq 4 and the atomic correlation energies[33] for B (−0.125 au), C (−0.158 au), and O (−0.258 au), we can derive the total molecular correlation energy of $E_{BH_3CO}(\mathrm{corr}) = -0.75 \pm 0.01$ au. Moreover, if we decompose the BH_3CO molecular extra correlation into parts corresponding to BH_3 and CO, then we can identify the remainder

$$\Delta E_{B\text{-}C}(\mathrm{corr}) = \Delta E_{BH_3CO}(\mathrm{corr}) - \Delta E_{BH_3}(\mathrm{corr}) - \Delta E_{CO}(\mathrm{corr}) \quad (6)$$

with formation of the molecular complex. Using eq 5 again, we estimate $\Delta E_{BH_3}(\mathrm{corr}) = -0.069 \pm 0.005$ au and $\Delta E_{CO}(\mathrm{corr}) = -0.115 \pm 0.003$ au. Thus, we obtain $\Delta E_{B\text{-}C}(\mathrm{corr}) = -0.03 \pm 0.01$ au for the correlation energy contribution to $-\Delta E(1)$, the energy change associated with reaction 1. (The uncertainties represent crude guesses of confidence limits.)

In Table IV we list total energies for species involved in reactions 1-3. The earlier ab initio calculations report values of 22.7,[10] 10.4,[9b] and 24.2[8] kcal/mol for ΔE of reaction 1, in drastic disagreement with the present estimated Hartree-Fock value of 6.4 kcal/mol (Table IV). The use of smaller basis sets and slightly different geometries[8,10] are probable roots of the discrepancies. (Our minimal STO and double-ζ Gaussian basis sets yield 4.0 and 8.1 kcal/mol for reaction 1, respectively. The results in ref 8 and 10 point to possible basis set imbalance problems and subsequent loss of accuracy when ΔE is obtained as a small difference between large numbers.) Our "experimental" data are taken from the sources listed in ref 23 and in footnotes to Table I of ref 31. However, not all of the figures dependent on experimental data may be significant, and we caution the reader to expect uncertainties as large as 5 kcal/mol, which is for instance the approximate discrepancy in ΔE found for reactions 1-3 from thermochemical[23] and appearance-potential[24] measurements. The ΔE's quoted in Table IV do show the importance of electron correlation in determining the heats of these particular reactions.[34] In every case, $\Delta E(\mathrm{corr}) > \Delta E(\mathrm{HF})$.

We have attempted to analyze $\Delta E(\mathrm{corr})$ in terms of the electron-pair model proposed by Snyder[35] for reactions between closed shell molecules, but have been able to do so with only modest success. For example, Snyder writes

Table IX. Borine Carbonyl Localized Molecular Orbitals (LMO's) Relative to the (2s1p/1s) STO Basis Set

	B_{1s}	C_{1s}	O_{1s}	O_{lp}	BC	BH[a]	CO[a]
1s H_1	0.0326	−0.0071	0.0005	0.0048	−0.0501	0.5854	−0.0388
1s B	−1.0093	−0.0037	0.0001	0.0048	−0.0358	−0.0526	−0.0026
2s B	0.0172	0.0022	0.0045	−0.0002	0.0138	0.2859	−0.0163
$2p_z$ B	−0.0134	0.0026	0.0006	−0.0229	0.2056	0.0973	0.0029
1s C	−0.0028	−1.0155	−0.0028	−0.0306	−0.0788	0.0051	0.0336
2s C	0.0157	0.0753	−0.0016	0.1914	0.7548	−0.0887	−0.1164
$2p_z$ C	0.0174	−0.0286	0.0165	0.2126	−0.5018	0.0284	−0.1725
1s O	0.0002	−0.0025	−1.0207	0.0726	0.0107	−0.0111	0.0449
2s O	0.0022	0.0091	0.1182	−0.8368	−0.0555	0.0148	−0.3147
$2p_z$ O	0.0027	−0.0328	0.0264	−0.0632	0.0852	−0.0137	0.2590
1s $H_{2,3}$						−0.0349	0.0173
$2p_x$ B						0.4019	−0.0342
$2p_x$ C						0.1111	0.3878
$2p_x$ O						−0.0881	0.6250

[a] The LMO's for the other two BH and two CO banana bonds are related to the LMO's quoted here by 120 and 240° rotations.

Table X. sp^n-Hybridization Coefficients of Boron Atomic Orbitals in BH_3CO

Case	Tetrahedral	Exptl[a]	Localized[b]	Trigonal
θ	109°28′	113°52′	118°34′	120°
sp^n	sp^3	$sp^{2.47}$	$sp^{2.09}$	sp^2
B_{2s}	0.5000	0.5367	0.5687	0.5774
B_{2p_z}	−0.2887	−0.2128	−0.1935	0.0
B_{2p_x}	0.8165	0.8165	0.7994	0.8165

[a] The coefficients were generated by assuming the hybrids point directly at the H atoms with the molecule in its equilibrium geometry, and by using the general relationship for sp^n, where $\theta = -s^{-1}$, n yields the normalized hybrid $(n + 1)^{-1/2}[\phi_{2s} + \sqrt{n}\ \phi_{2pj}]$. [b] The values of θ and n were computed by using the coefficients of the boron, 2s, $2p_z$, and $2p_x$ orbitals (renormalized to one) from LMO number 6 of Table IX.

Table XI. LMO Contributions to the Dipole Moment of BH_3CO (au)[a]

LMO	B origin	C origin
Oxygen 1s	−10.0571	−4.2367
Carbon 1s	−5.7883	+0.0319
Boron 1s	−0.0669	+5.7534
Oxygen *l*p	−6.3161	−0.4957
B-C bond	−4.8828	+0.9376
Banana bonds	−24.6470	−7.1860
B-H bonds	−3.3130	14.1479
Total electronic	−55.0712	8.9524
Total nuclear	56.1345	−7.8891
Net moment	1.0633	1.0633

[a] 1 au = 2.5415 D. The values quoted here are based on the minimal (2s1p/1s) STO basis set in Table IIA.

$$\Delta E_{corr}(3) = -6(b^2/b'^2) - 4(1s^2/val) \tag{7}$$

where the bond-other-bond (b^2/b'^2) and core-valence ($1s^2$/val) correlation energies are given empirical values of −0.0118 and −0.0027 au, respectively, and lead to $\Delta E_{corr}(3) = 51.2$ kcal/mol. Even allowing for sizable error limits in Table IV, we conclude that a more complete model of correlation corrections is needed for reaction 3, such as that given by Ahlrichs[36a] who obtains $\Delta E(3) = 36$ kcal/mol and $\Delta E_{corr}(3) = 15.7$ kcal/mol using the coupled electron-pair approximation with a basis set of slightly better quality ($E_{B_2H_6} = -58.82699$ au) than our best basis. His result[36a] of 20.7 kcal/mol at the Hartree-Fock level [$\Delta E_{SCF}(3)$] is in reasonable agreement with our value reported in Table IV. Dixon, Pepperberg, and Lipscomb[36b] used a minimal STO basis set with CI including all single and double excitations from the valence shell to obtain $\Delta E(3) = 16.9$ kcal/mol with $\Delta E_{SCF}(3) = 7.5$ kcal/mol and $\Delta E_{corr}(3) = 9.4$ kcal/mol. The fact that they recovered approximately half of the SCF *and* correlation contributions suggests that basis set limitations present problems at *both* levels of approximation. Nevertheless, one might hope that Snyder's model for the BC bond formation in reaction 1 would distinguish between bonding and nonbonding pair forces and would facilitate our understanding of correlation effects for this class of molecular complexes. Unfortunately, both types of pairs yield $\Delta E_{corr}(1)$'s that are in order of magnitude disagreement with the data in Table IV, and point again to the need for a more sophisticated analysis.

We therefore turn to other means for probing the nature of the formation of the BH_3CO complex. A first indication of the bonding interaction may be observed in the molecular orbital energies ϵ from our largest GTO basis set for BH_3CO and BH_3 and CO molecules as given in Table V. While the deformation of CO shows negligible effects, the change in BH_3 from planar to pyrimidal forms indicates a tendency for the 1e and $3a_1$ MO's to destabilize. The accompanying deformation energies are 0.3 and 13.7 kcal/mol for CO and BH_3, respectively. This may be compared with the stabilization energy of BH_3CO of 6.4 kcal/mol (Table IV). The lowest virtual orbitals of BH_3 and CO are seen to be of $3a_1$ and 2π symmetry, with the former approximately a factor of 3 lower. This is consistent with earlier analyses[2,8,10] that attribute the bonding in BH_3CO to interaction of the 5σ MO of CO with the vacant $3a_1$ MO of BH_3 and a concomitant, but smaller, interaction of the 1e MO of BH_3 with the vacant 2π MO of CO. This supports Mulliken's[2] categorization of CO as an "amphodonor", that is, a molecule with both electron donor and acceptor capabilities. The core ϵ's in BH_3CO indicate that the 1s electrons of carbon and oxygen are more tightly bound than in free carbon monoxide, whereas the boron 1s electrons are somewhat less tightly bound. This information, taken with similar apparent stabilization effects for the $4a_1$ MO, shows that the CO bond in BH_3CO is somewhat stronger than in free CO. This may be attributed to the use of the 5σ MO of CO, which is antibonding in nature, in a bonding interaction with the $3a_1$ MO of BH_3. Conversely, electron transfer from the 1e MO of BH_3 into the 2π MO of CO shows a slight destabilization in the 2e MO of BH_3CO since bonding electrons in BH_3 move toward the CO end.

Population analyses for the four BH_3CO wave functions described earlier are given in Table VI. Overall, they show similar trends but the absolute magnitudes differ considerably. In particular, the minimal STO basis set assigns a positive charge to the boron atom, even though the BH_3 fragment taken as a whole is negative. The polarization functions are seen to increase the transfer of electrons from the CO to the BH_3 end and also show the tendency for migration of electrons to the H atoms. The overlap populations indicate that the strongest bonds are, of course, between C and O and B and H. The B to C bond is somewhat less than half as strong as that of B to H, which may be considered a normal single bond. The overlap populations between the remaining atoms in the system are all negative and relatively small.

The changes occurring in the formation of the BH_3CO complex are also manifested in terms of population analyses as shown in Table VII. The gross atomic and overlap populations have been broken down into the portions due to the a_1 or σ and e or π MO's to better exhibit the interactions. The gross atomic population of the boron atom in BH_3CO is seen to gain electronic charge in the a_1 MO's and lose charge in the e MO's relative to isolated BH_3. A similar but opposite effect is seen for carbon. The oxygen atom is not much affected by the complex formation, suggesting that the process is localized at the carbon end of CO. The H atoms show an increase in electron population from the a MO's and a decrease from the e MO's.

The overlap populations show similar trends. Complex formation increases the CO overlap by a factor of 2 in the σ MO's and decreases it slightly in the π MO's. The B-C bond overlap populations from the a_1 and e MO's are about equal. The importance of the latter MO's is enforced also by a positive overlap between the e MO's of C and H even though the total C-H overlap is negative. These results indicate that hyperconjugative stabilization is relatively important in BH_3CO. While this conclusion is in qualitative agreement with earlier minimal STO basis set calcula-

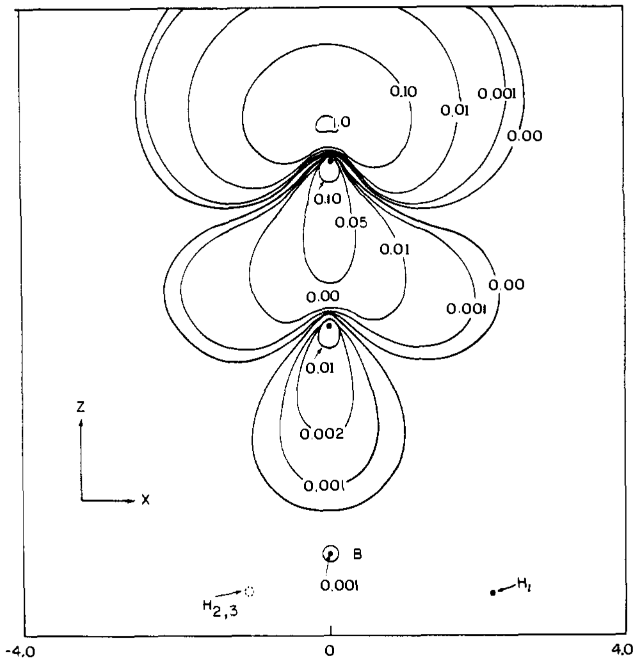

Figure 1. Oxygen-lone-pair orbital in the xz plane. Density contours in units of e/a_0^3 for one electron.

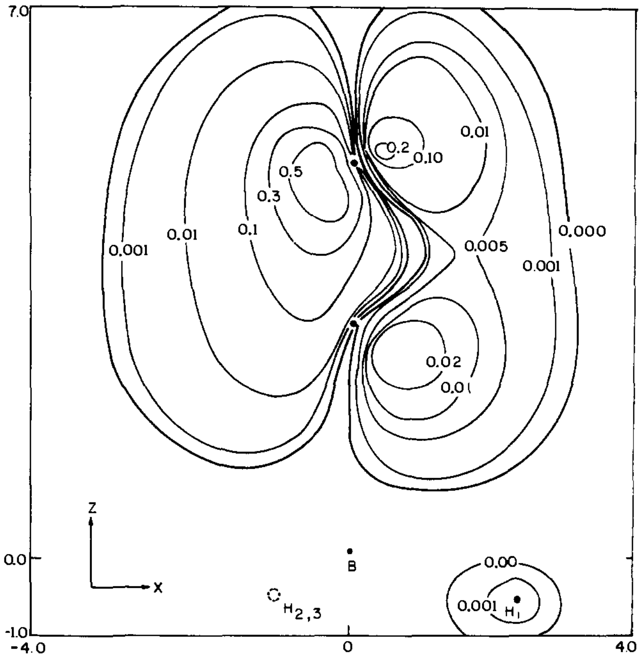

Figure 2. LMO banana-bond density contours in the xz plane and in units of e/a_0^3 for one electron.

tions,[8,10] the increased basis set size, particularly the addition of polarization functions, seems to improve the bonding environment for the complex and enhance the importance of hyperconjugation.

This charge rearrangement is reflected to some extent in all of the properties listed in Table VIII, especially in the dipole moment μ_z along the threefold (z) axis, and in the electric fields **E** and their gradients **q** at the heavy-atom positions. We can obtain some absolute measure on the accuracy of our wave functions by comparing these quantities, or those derived from them, with experiment or with purely theoretical conditions that exact Hartree-Fock wave functions must satisfy. Turning first to μ_z, which is indeed directed B^{-}-C^{+} as the net charges suggest, we find that the Slater minimum basis-set function yields a moment that is too large by a factor of 1.5 from the experimentally determined value[4] of 0.7062 au (1.795 D). Addition of polarization functions reduces the calculated value to the point where our most refined GTO basis comes within less than 4% of reproducing the measurement. Components of the electric field vector can perhaps be summarized best in the sum of forces $\mathcal{F}$ over all the nuclei which should equal zero[37] in all directions if the basis set is complete (Hartree-Fock limit) and the geometry has been optimized. For BH_3CO, the x- and y-force sums are zero by symmetry; however, we see that $\langle \mathcal{F}_z \rangle$ is indeed sensitive to basis set and decreases by nearly an order of magnitude from left to right in Table VIII, showing again the substantial improvement that can be attributed to the polarization functions.

The only other property for which we have experimental data is the ^{11}B quadrupole coupling constant $(eq_{zz}Q_B)/h$ that was discussed by Das[11] in a semiquantitative manner using valence-theory arguments about bonding in the molecule, and in the measurements of Gordy, Ring, and Burg[5] who report $(eq_{zz}Q_B)/h = 1.55 \pm 0.08$ MHz. If we now use Nesbet's[38] value for the ^{11}B nuclear quadrupole moment $Q_B = 0.04065 \pm 0.00026$ b, we find $\langle q_{zz} \rangle_B = 0.16 \pm 0.01$ au. The discrepancy between this and our best calculated value of 0.22 au is probably due to residual basis set inadequacy, though correlation or vibrational effects may also be partly responsible. Additional d functions on the heavy atoms, d functions centralized in the core region of the B atom, and perhaps p orbitals on H to maintain balance would be worthwhile in future work. The remaining properties in Table VII have not been subject to experimental tests, but they too appear to have converged reasonably well within the Hartree-Fock approximation.

The output of Hartree-Fock self-consistent-field calculations is a set of canonical MO's that are delocalized over the entire molecule. Although such a description is very useful for some purposes (e.g., discussion of electronic transitions), a physical interpretation of bonding in terms of directed valence theory is often obscure. One method of extracting this information is to transform the orbitals in such a way as to maximize the intra-orbital repulsion energies as was suggested by Edmiston and Ruedenberg (ER).[39] The result is a description of the electron distribution that resembles the traditional concepts of "lone pairs", "pair bonds", and "inner-shells". As is known, because the transformation between the two descriptions is unitary, values of one-electron properties are unchanged.

Minimal basis set wave functions have traditionally been used for analyses in terms of valence theories. In general, the level of sophistication is sufficient to expose the qualitative features. Accordingly, we transform the canonical (2s1p/1s) MO's into localized forms (LMO's).[25,26] The STO coefficients for each LMO given in Table IX may be classified in seven categories: boron 1s, carbon 1s, oxygen 1s, oxygen lone pair, BC bond, BH bonds, and CO "banana" bonds. These coefficients can be used to generate electron density maps that display pictorially the most prominent features of each LMO.

Figures 1-3 illustrate the CO bonding in BH_3CO. It is very instructive to compare them with the maps of England, Salmon, and Ruedenberg[40] for an isolated carbon monoxide molecule because they show only minor differences. As one might expect, all of the C and O inner-shell orbitals are indistinguishable, and even the oxygen lone pair (Figure 1) is virtually identical with that in carbon monoxide. The CO "banana bonds" (Figure 2) show a slight tendency to delocalize onto the hydrogen atoms, but are only somewhat less shifted in the direction of the oxygen atom than in carbon monoxide. A cut through the CO bond perpendicular to the

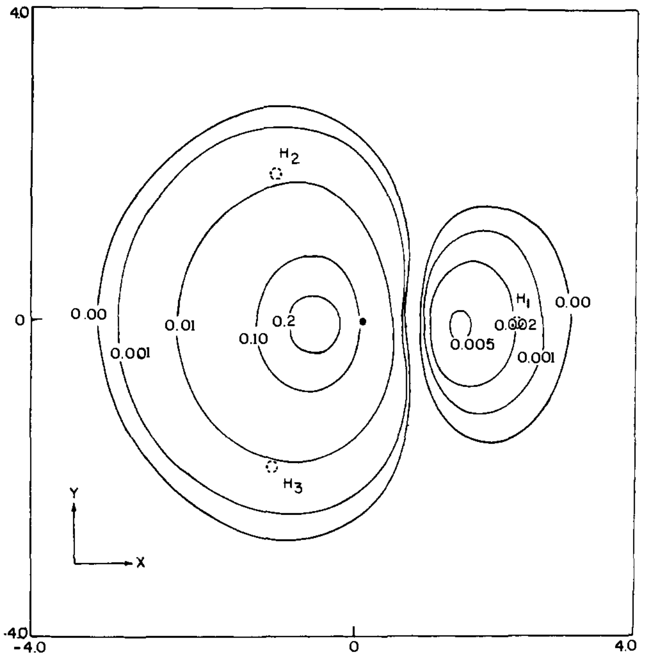

Figure 3. Cross section of the banana orbital in Figure 2 parallel to the xy plane and bisecting the CO distance. The other two banana orbitals (not shown) are identical with this one but are rotated by 120 and 240°, respectively. Density contours are in e/a_0^3 for one electron.

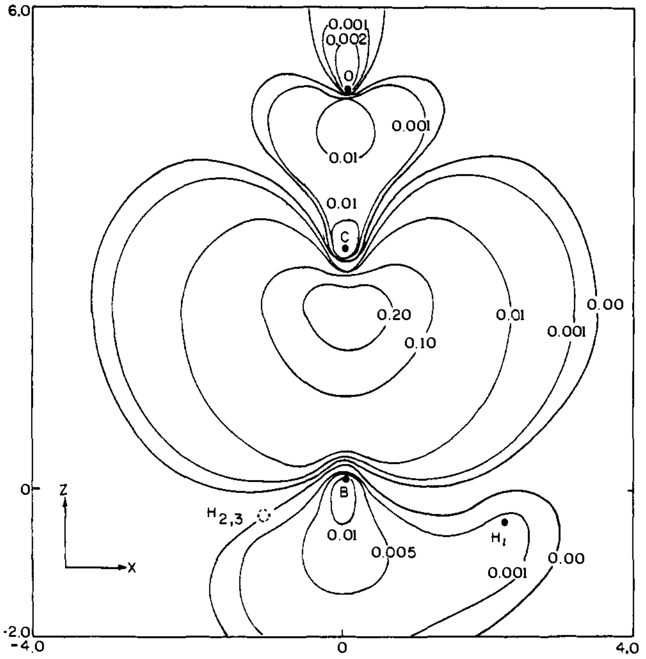

Figure 4. Boron-carbon LMo density in the xz plane and in units of e/a_0^3 for one electron. The hydrogen atom labeled H_1 is in the plane, whereas H_2 and H_3 are above and below it as indicated by the dotted circle.

internuclear axis (Figure 3) shows that the region of maximum electron density lies between the H_2 and H_3 atoms. This preferential conformation of the "banana bonds", "trans" relative to the BH_3 fragment, was not found when the ER procedure was employed. It is surmised that interaction between the BH bonds and the "banana" bonds is so small that the 2 × 2 rotations employed in this method could not lead to an absolute maximum of the self-energy. The procedure used here was devised by Taylor and Liang[25,26] and utilizes the method of principle ascents in treating all of the canonical MO's in a single diagonalization per cycle, thereby circumventing the problems inherent in the 2 × 2 method. The resultant LMO's for BH_3CO are identical with those generated using the ER method with the exception that the "banana" bonds *are* oriented *trans* to the BH_3 fragment. (The ER procedure was found to yield this result if these LMO's are used as starting guesses.)

The boron-carbon bond (Figure 4) has the appearance of a distorted carbon lone pair when compared with carbon monoxide.[40] In the course of exploring a potential energy surface for BH_3CO, using the minimal STO basis set, it was found that the optimum boron-carbon internuclear distance is 0.41 bohr longer than the experimental R_{BC} of 2.91 bohr. The other geometric parameters were all within 4% of the experimental values. Although the surface is extremely flat in the B-C direction, it appears from Figures 4 and 5 that a longer R_{BC} would be more favorable to back-bonding by the H atoms into the vacant CO 2π MO.

The boron-hydrogen bond (Figure 5) seems to support the suggestion that part of the attractive interaction between the CO and BH_3 fragments in BH_3CO can be attributed to overlap of the carbon "banana" bonds and the boron-hydrogen bonds. The electron density around the hydrogen atom is somewhat delocalized toward the BC-bond region and takes on the appearance of a three-center bond.

The three BH bonds may be discussed in terms of sp^n hybridization. Here, $n = -s\ \theta$ where θ is the angle between equivalent hybrid lobes. A comparison among the sp^3- and sp^2-hybridization coefficients shows those predicted by the geometry of BH_3CO lead to $sp^{2.47}$ hybridization whereas the LMO's yield $sp^{2.09}$. The increase in θ between the hybrid lobes suggests that the BH_3 fragment seeks to retain its planar (sp^2) form considerably more than the equilibrium geometry indicates.

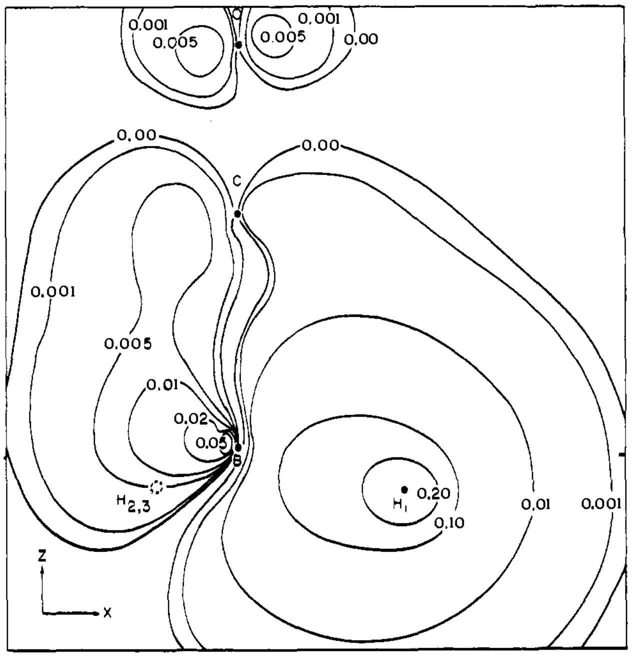

Figure 5. LMO-BH_1 density in the xz plane and in units of e/a_0^3 for one electron. The hydrogen atom positions are the same as in Figure 4.

The LMO description of BH_3CO supports the contention that the molecule is essentially two identifiable fragments which interact weakly through a dative BC bond. The fact[6] that the vibrational frequencies involving motion of the BH_3 fragment relative to the CO fragment are small in comparison to other modes lends further credence to this picture.

Our interpretation of the bonding in BH_3CO has been in terms[2] of "whole-complex MO's". It is also possible alternatively to use the resonance-structure concept and write[2] the molecular wave function as

$$\Psi = a\Psi_0(\mathrm{OC, BH_3}) + b\Psi_1(\mathrm{OC^+\text{-}BH_3^-}) + c\Psi_2(\mathrm{OC^-\text{-}BH_3^+}) \quad (8)$$

where the Ψ_0 is the so-called no-bond structure, Ψ_1 represents the n-donor action of the CO and v-acceptor action of BH_3, and Ψ_2 describes the hyperconjugative action of BH_3 as a quasi-π donor into the vacant 2π MO of CO. [BH_3 is sometimes designated a "b acceptor" because of the presence of the third term in eq 8.] Examining Figures 4 and 5, it appears that $b > c$ for the reasons that we have already discussed. In fact, this is in agreement with Gordy, Ring, and Burg,[5] with Mulliken and Person[2] (who conclude also that $a > b > c$), and with Kato et al.[8] (who report values of $a = 0.548$, $b = 0.298$, and $c = 0.147$ based on their minimal basis set plus CI calculations).

The origin of the dipole moment can be examined more quantitatively using the data in Table XI where individual LMO contributions are given for two origins of the coordinate vector. Taking boron as origin, for instance, and assigning two units of nuclear charge to each LMO, it is found that the B-H bonds (−5.02 au) subtract somewhat less than the oxygen lone pair (3.78 au), the B-C bond (0.94 au), and the banana bonds (1.36 au) collectively, and with the latter positive contributions determining the net sign.

Further analysis of the BH_3CO molecule is being carried out[41] using the energy decomposition scheme of Iwata and Morokuma[42] who expressed the total energy in terms of electrostatic, polarization, exchange, and charge-transfer contributions. In this manner it is hoped that the nature of the bonding interaction can be assigned more clearly to chemically identifiable contributions. The net stabilization of the complex due to hyperconjugation[12b] may also be quantitatively defined. The location of possible charge transfer and other excited states of the complex, potential energy surfaces, and the effects of electron correlation should be investigated in future work.

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