Theoret. chim. Acta (Berl.) 10, 193—208 (1968)

Theory of Electronic Effects in the Formation of the Trimethylamine-Trimethylboron Addition Complex*

S. EHRENSON

Chemistry Department, Brookhaven National Laboratory, Upton, N.Y. 11973

Received November 2, 1967

The Lipscomb MO method has been employed to examine various electronic properties of the $(CH_3)_3B + N(CH_3)_3$ addition reaction. Results obtained indicate previous empirical notions concerning dative hyperconjugative stabilization in the boron reactant and its loss in the adduct are substantially correct. Charge flow accompanying donation by nitrogen of its lone pair in formation of the adduct also follows classical expectations. Combination with perturbation theory allows computation of zero-point energy secondary deuterium isotope effects upon equilibrium position. These effects in the boron methyls agree well with experiment; similar effects are predicted to be absent for amine methyl substitution. Other experimentally verified properties of the reactant and product molecules are also correlated with the theoretical results.

Das MO-Verfahren nach Lipscomb wurde zur Untersuchung der Additionsreaktion $(CH_3)_3B + N(CH_3)_3$ herangezogen. Die Ergebnisse zeigen, daß die empirischen Vorstellungen bezüglich einer Stabilisierung infolge Hyperkonjugation und deren Nachlassen im Addukt richtig sind. Auch die Ladungsübertragung, die mit dem teilweisen Übergang des einsamen Elektronenpaares vom Stickstoff einhergeht, folgt der klassischen Erwartung. Mittels Störungsrechnung läßt sich die Auswirkung des sekundären Deuterium-Isotopieeffektes auf die Lage des Gleichgewichtes berechnen. Dabei ist die Übereinstimmung mit dem Experiment in bezug auf die Boran-Methylgruppen gut; außerdem läßt sich voraussagen, daß ähnliche Effekte bei den Amin-Methylgruppen nicht auftreten. Andere experimentell nachgeprüfte Aussagen über Ausgangs- und Endprodukte sind ebenfalls mit der Theorie im Einklang.

La méthode O. M. de Lipscomb a été utilisée pour étudier différentes propriétés électroniques de la réaction d'addition $(CH_3)_3B + N(CH_3)_3$. Les résultats obtenus indiquent que les notions empiriques antérieures concernant la stabilisation par liaison dative et hyperconjuguaison dans le réactif boré et la perte de cette stabilisation dans le produit d'addition sont foncièrement correctes. La migration de charge accompagnant le don de sa paire libre par l'azote lors de la formation du produit d'addition est conforme aux prévisions classiques. La théorie des perturbations permet le calcul des effets isotopiques secondaires du deutérium sur la position d'équilibre. Ces effets sont en bon accord avec l'expérience pour le méthylbore; de tels effets ne doivent pas se produire pour la substitution méthylique de l'amine. D'autres propriétés vérifiées par l'expérience pour les molécules réagissantes et le produit sont corrélées de même avec les résultats théoriques.

Introduction

The recent development of semi-empirical MO methods for treatment of large molecules derived from rigorous self-consistent-field (SCF) calculations on related small molecules have provided the means for profitable reexamination of many ostensibly closed questions concerning electronic effects on chemical reactivity. What appears to be a particularly useful and promising method for future use is the kinetic-energy-separated extended Hückel-type method developed by Lipscomp and co-workers [1]. Described here is a straightforward application of this method to the chemical equilibrium,

$$(CH_3)_3B + N(CH_3)_3 \rightleftharpoons (CH_3)_3B - N(CH_3)_3$$

---

* Research performed under the auspices of the U.S. Atomic Energy Commission.

in order to examine, in terms of the theory, the following specific questions which have in the past received only very qualitative answers.

What is the effect of dative isovalent hyperconjugation (HCJ) upon the electronic distribution in boron trimethyl and how are these effects moderated upon formation of the complex? The pertinence of this issue can be fully appreciated upon realization that this is the premier system for expected exhibition of HCJ effects where only neutral reactant and product ground state species are involved.

What is the role of the amine in complex formation? Does it suffice to describe this reactant solely in terms of its ability to donate the nitrogen lone pair, or are there other features of importance, for example, concerned with the mode of electron donation by its substituent methyl groups?

Subsidiary points such as the additional inductive π- and σ-charge shifts expected to accompany dative HCJ donation to boron, and whether β-secondary isotope effects of any size are to be expected from the electronic rearrangements accompanying complexation (in the nitrogen as well as the boron methyls) are also pertinent.

The preceding all relate to the specific chemical equilibrium under investigation. Other matters useful in the understanding and possible refinement of the theoretical method are expected to, and do arise from its application to this system. Several such points will be considered in detail in an accompanying paper, in particular, the question of charge redistribution in coulombically unbalanced systems. Generalized extensions and meshing of the present and complementary theoretical methods to obtain quantitative estimations of such properties as β-secondary hydrogen isotope effects will be attempted here. Correlations are also drawn where possible with other experimental evidence such as quadrupole coupling constants in trialkyl boron compounds and addition equilibrium position and molecular geometries for this and related reaction systems.

Theory, Parametrization and Molecular Geometries

The LCAO MO approximation developed by Lipscomb et al. [1] as an improvement of the extended Hückel method was adopted for all the MO calculations to be described. The method has the primary virtue of recognizing generality of proportionality between the potential energy part (M_{ij}) of the off-diagonal SCF Hamiltonian matrix element (F_{ij}) and the product of the overlap integral with the average of the pertinent diagonal potential energy matrix elements. This provides a means of synthesis of the eigenvalue matrix from rigorously obtained theoretical results for similar, simpler molecules through the following relationships,

$$F_{ij} = T_{ij} + M_{ij}, \tag{1}$$

$$M_{ij} = K_{ij} S_{ij} (M_{ii} + M_{jj})/2. \tag{2}$$

The matrix elements are as defined in the SCF formulation [2] (M replaces the potential energy UMATRIX notation) and K_{ij} is essentially constant over a variety of atom-atom two center interactions, being dependent only upon the nature of the Slater orbitals, i and j.

This method represents an improvement of the Mulliken [3], Wolfsberg-Helmholz [4] approximation, which has recently been exploited through automatic computation methods by Hoffmann and Lipscomb [5], where proportionality is assumed, on more or less pragmatic grounds, between the entire off-diagonal and averaged diagonal Hamiltonian matrix elements. The superiority of the separated matrix element proportionality approximation is amply demonstrated in Ref. 1. At the same time, a disadvantage of sorts exists in the Lipscomb method in that SCF values for F_{ii} are required, rather than the more readily obtainable valence state ionization potentials used in the earlier methods. In general then, the potential energy proportionality method will always require prior single Slater orbital SCF results for molecules containing the atoms of interest in their proper valence states. This is not judged a major problem here, at least at the outset, in that all the atoms of interest have been investigated in some detail as primary subjects upon the results of which the theory was built. Whether all atoms are here as similar to their respective standards as one could desire is a question upon which the initial results obtained will hopefully bear. The MO parameters employed and their origins are shown in Table 1.

The molecular geometries for the reactants were taken from Sutton's Tables of Interatomic Distances [6] with heavy atom framework distances and angles accepted as quoted. All methyl group C–H angles and distances were taken as tetrahedral and 1.09 Å respectively, the latter close in accord with Lipscomb's recommended distances and under the assumption that the original determinations

Table 1. *Molecular orbital parameters*

A. α's (F_{ii}'s) and orbital exponents[a]

Orbital	Exponent	α	Orbital	Exponent	α
B1s	4.700	−7.706	N1s	6.700	−15.519
2s	1.300	−1.081	2s	1.950	− 1.859
$2p_{x,y}$	1.300	−0.337[b]	$2p_{x,y}$	1.950	− 0.334[b]
		−0.286[c]			− 0.328[d]
$2p_z$	1.300	−0.337[b]	$2p_z$	1.950	− 0.334[b]
		−0.439[c]			− 0.356[d]
			C1s	5.700	−11.284
H1s	1.200	−0.537	2s	1.625	− 1.463
			2p	1.625	− 0.364[b]

B. Coefficients for the M_{ij} relationship (Eq. 2)[e]

Two center K_{ij}

1s—2s	0.81	1s—H	0.83
1s−2p	0.82	2s−H	1.05
2s—2s	1.02	2p—H	0.98
2s—2p	1.06		
2pσ—2pσ	1.05	H−H	1.18
2pπ—2pπ	0.73[f]		
K_{1s-2s} (1 Center)	0.66	Zero-overlap K	0.40

[a] α-values in a.u. [b] Averaged $2p\alpha$ values from diborane, ammonia and ethane SCF calculations as recommended by Lipscomb. [c] Anisotropic $2p\alpha$'s taken from B_2H_6 SCF with averaged $2p_x$ and $2p_y$. [d] From NH_3 SCF calculation. [e] General K's suggested in Ref. 1, Part III. [f] For π-quasi-π and quasi-π-quasi-π interactions. No π-π interactions present in the system of interest.

of these distances were not entirely trustworthy or represented no more than input guesses by the original investigators for purposes of structural determination simplification. An additional reason is to simplify various tests for conjugation and hyperconjugation changes accompanying reaction.

Specification of the structure of the adduct requires a more serious degree of assumption. While the adduct has been studied more recently and by a potentially more powerful method (by microwave spectroscopy versus electron diffraction for the reactants, all species in the gas phase), the study was grossly incomplete. From a single observed moment of inertia, Lide et al. [7] predicted a remarkably long B–N bond length (1.80 ± 0.15 Å) on the assumption that the boron-methyl and nitrogen-methyl bond lengths remain the same in the adduct as in the reactants. In a later exchange of views [8] with Geller [9] based mainly on analogy arguments from the known behavior of other boron and nitrogen adducts, an apparently more reasonable range of structures was agreed upon. The studies of primary interest here will employ one of the compromise structures; some attention will be paid however to the effects of adopting the original structure characterized by the long B–N bond.

Table 2. *Bond distances and angles*[a]

$B(CH_3)_3$: Electron diffraction, gas		
Planar symmetrical framework, CBC angle 120 ± 3[c]		
C–B distance	1.56 ± 0.02	
C–H	1.05[b]	(1.09)
HCH angle	tetrahedral	
$N(CH_3)_3$: Electron diffraction, gas		
Skeletal symmetry C_{3v}[c]		
C–N distance	1.47 ± 0.01, 1.472 ± 0.008	(1.47)
C–H	1.06[b]	(1.09)
CNC angle	108 ± 4, 108.7 ± 1.0	(1.08)
HCH	tetrahedral	
$(CH_3)_3BN(CH_3)_3$: Microwave absorbtion, gas[d]		
Skeletal symmetry C_{3v}[c]		
C–B distance	1.56, 1.65	(1.65)
C–N	1.47, 1.50	(1.50)
B–N	1.80, 1.65	(1.65, 1.80)
CBC and CNC angles	109.5, 105–107	(105.5)
HCH	tetrahedral	

[a] All distances in Å, angles in degrees. Values in parentheses adopted here if value is controversial. [b] Assumed in structural determinations. [c] The methyl groups are assumed to lie so that the dihedral angle between one CH bond of each methyl and the symmetry axis of the molecule, pointing in the pyramidal species toward the hydrocarbon end of the framework, is zero degrees. [d] First set from Ref. 7, second from Refs. 8 and 9 as range of compromise values.

All computations were carried out on a CDC 6600 computer, programmed in FORTRAN IV. Two main programs were used, the first for generation of the molecular Cartesian coordinates from the bond length and angle information presented in Table 2, the second for completely automatic generation of the matrix elements for, and eigenvalue-vector solution of the molecular orbital matrices. Integral calculations in the latter program were accomplished through a generalized A- and B-function generator to give the overlap integrals, S_{ij}; the kinetic energy integrals T_{ij} were then obtained from the appropriate S_{ij}'s [10]. All or any part of the complete Mulliken population analysis scheme [11] could be automatically applied to the eigenfunctions derived. The Cartesian coordinates as generated by the first program for the three molecules of interest and the MO parameters of Table 1 constitute the input for the second program.

The alkylborane, amine and adduct are positioned so that the Cartesian X- and the C_{3v} rotation axes are identical. One of the three carbon-heteroatom bonds for each species (or adduct fragment) is positioned in the XZ plane; the methyl groups are taken to be staggered in the adduct. One hydrogen of each methyl is assumed to lie in the plane defined by the C_{3v} axis, the heteroatom and the carbon to which it is attached and, in the pyramidal species, is located below the triangular base defined by the carbons. All other atom positions are defined by these and the overall molecular symmetries.

Results and Discussion

1. Molecular Energies

Tables 3 and 4 contain summaries of the most important MO results obtained for the species involved in the addition equilibrium. For the Table 3 calculations, the isotropic $2p\alpha$ approximations suggested in Ref. 1 for the nitrogen and boron atoms, as well as for carbon, were employed. In Table 4 the results obtained by direct application of the $2p$ diagonal matrix elements obtained in the SCF calculations on B_2H_6 and NH_3 (second set of Table 1) are shown.

The energy quantities displayed are, in order, one-half the total orbital electronic energies, binding energy and total energy. The latter two are obtained as in Ref. 1. Also shown are the energies of the highest filled molecular orbitals (HFMO) for each molecule. From the E_{tot} difference (product minus reactants) an estimation of the energy of addition is obtainable which may be compared with experiment. Similarly, the Koopman's theorem values for the ionization potentials are directly available from the HFMO results.

While these results must be judged as qualitatively satisfactory, it is quickly apparent they are not in quantitative agreement with experiment. The stabilization energy accompanying addition is overestimated and the ionization potentials are found, where comparisons with experiment are possible, to likewise be in error. The former values is ~ 0.2 a.u. or on the order of 100 kcal/mole, independent of the parameterization choice, which would imply the addition reaction to be virtually complete. Experiment suggests the equilibrium would lie strongly but not as completely in this direction ($\Delta H = -17.6$ kcal/mole, $\Delta S = -45.7$ eu for addition) [12]. The HFMO results from the isotropic $2p\alpha$ calculations are ~ 2 eV in error compared to the observed IP's, being high for $B(CH_3)_3$ and low for $N(CH_3)_3$, although the ordering of the potentials and the orbital origins of the ionized electrons are in agreement with expectation. When the non-isotropic $2p\alpha$ set is employed these discrepancies are reduced by about one-half.

The differences noted with experiment are not surprising. To the degree of accuracy required for meaningful correlations, all the individual molecule quantities examined thus far are quite sensitive to parameter choice, especially to the $2p\alpha$ values of the heteroatoms, as a comparison of the first entries of Tables 3 and 4 quickly reveals. The comments of Lipscomb in paper III of Ref. 1 are pertinent to discrepancies generally noted for IP's. Errors of similar magnitude are often obtained from this and more rigorous MO methods. The stabilization energy for addition suffers the additional disadvantage of being the very small difference of two extremely large numbers, as is the wont of such a quantity theoretically derived without benefit of scaling against empirical results for a similar reaction system. The charge density and bond order quantities, to which attention is next directed, do not suffer the last disadvantage and need not in general be known to the absolute or relative accuracies required of the energies. A realistic appraisal of how sensitive these quantities are to parameter variation and, therefore, how reliable the answers which are generated from their use may be to the questions posed in the Introduction, is expected from the results on the two parameter sets here considered.

Table 3. *Molecular orbital results*[a]

	$(CH_3)_3B$	$N(CH_3)_3$	$(CH_3)_3B\text{-}N(CH_3)_3$[b]	
Energies				
$-1/2\,\Sigma\,\varepsilon_i$	49.1478	57.8060	107.1729	
$-A$	1.443	1.182	2.844	
$-E_{\text{tot}}$	143.308	172.808	316.336	
HFMO	−0.383[c,d]	−0.244[e]	−0.372[c]	
Central atom net atomic and orbital charges, q				
$p_z(\pi)$[f]	−0.348	0.280	−0.661	0.934
p_x, p_y	0.397	0.048	0.306	0.054
Total	0.704	0.024	0.293	0.816
Methyl group charges, q				
$Cp\pi$[g]	0.000	−0.035	−0.053	−0.033
C Total	−0.525	−0.113	−0.594	−0.155
Avg. H	0.097	0.035	0.082	0.044
Overlap populations, methyl carbon-central atom, p[h]				
π-quasi-π	0.076	0.010	−0.013	0.000_2
quasi-π-quasi-π	−0.020	−0.006	−0.019	−0.004
Total	0.795	0.773	0.684	0.774
CH overlap populations, p[i]				
Total, 3H Avg.	0.747	0.7357	0.756	0.7365
πH	0.470, 0.115	0.500, 0.129	0.514, 0.128	0.506, 0.127
σH	0.082, 0.084	0.072, 0.079	0.079, 0.084	0.075, 0.077
B–N OP Total 0.679, $p\sigma$ 0.301, $p\pi_{\text{quasi}}$ −0.002				

[a] For the isotropic average $2p\alpha$, all energies in a.u. [b] When two numbers appear under this heading, the left refers to the boron end of the molecule, the right to the nitrogen end. [c] Doubly degenerate MO's. [d] The experimental I.P. by electron impact is −0.323, O. Osberghaus, Z. Physik **128**, 366 (1950); R. W. Law and J. L. Margrave, J. chem. Physics **25**, 1086 (1956). The energy of the lowest unfilled MO is −0.179. [e] The latest photoionization value is −0.289, L. D. Isaacs, W. C. Price and R. G. Ridley, Vacuum Ultraviolet Spectra and Molecular Ionization Potentials, in "The Threshold of Space", ed. M. Zelikoff, Pergamon Press, Ltd., London, 1957, pp. 143–151. [f] The orbital along the principal symmetry axis of the molecule, true MO π only for $B(CH_3)_3$. [g] The carbon p-orbital perpendicular to the bond with the central atom and coplanar with p_z. [h] For the amine and adduct, the π-π (perpendicular to the bond) components. [i] The carbon quasi-π and σ components along the C-central atom axis, see text.

Table 4. *Molecular orbital results*[a]

	$(CH_3)_3B$	$N(CH_3)_3$	$(CH_3)_3B\text{–}N(CH_3)_3$[b]	
Energies				
$-1/2\,\Sigma\,\varepsilon_i$	49.1360	57.8192	107.1812	
$-A$	1.431	1.195	2.852	
$-E_{tot}$	143.320	172.821	316.344	
HFMO	$-0.368^{c,d}$	-0.260^{e}	-0.360^{c}	
Central atom net atomic and orbital charges, q				
$p_z(\pi)^f$	−0.551	0.266	−0.771	0.963
Total	0.626	0.024	0.322	0.882
Methyl group charges, q				
$Cp\pi^j$	0.039	(−0.020)	(−0.066)	(−0.012)
C Total	−0.532	−0.115	−0.625	−0.158
Avg. H	0.108	0.036	0.083	0.044
Overlap populations, methyl carbon-central atom, p				
π-quasi-π^j	0.094	(−0.006)	(−0.027)	(−0.012)
Total	0.786	0.773	0.676	0.775
CH overlap populations, p				
Total, 3H Avg.	0.737	0.7365	0.755	0.7368
B–N OP Total 0.689, $p\sigma$ 0.317, $p\pi_{quasi}$ −0.001				

[a] For the B_2H_6 $2p\alpha$'s, π's averaged and NH_3 $2p\alpha$'s. Footnotes b–f of Table 3 apply. [j] Quantities shown in parenthesis are the $2p_z$ orbital charges and $2p_z-2p_z$ OP's which have not been resolved in terms of bond directions. The comparable values for Table 3 are for the charges −0.020, −0.059 and −0.012. For the OP's, −0.005, −0.024 and −0.011.

2. Atom and Orbital Population Charges

Examination of the charge population values for the methyl substituted atoms, lower sections of Tables 3 and 4, indicates boron to be a strong π-acceptor in trimethyl boron while being an over-all electron donor. This is in accord with expectation. The range of π-electron acceptance is from roughly 1/3- to 1/2-electron, dependent upon whether the boron $2p\pi\alpha$ is slightly electropositive compared to the corresponding carbon parameter (as in the isotropic set, i.e., −0.337 *vs.* −0.364 a.u.) or somewhat more electronegative (as in the second parameter set where B $2p\alpha_z$ is −0.439). The over-all boron donation varies considerably less with parameter variation (from 0.70 to 0.63, under the same change) which is doubtlessly due to an accompanying electronegativity decrease in the $2p\sigma$ α-values concomitant with the increase for $2p\pi\alpha$.

It is interesting to examine from whence these charges flow in the $B(CH_3)_3$ molecule. The quasi-π orbitals on the carbons capable of conjugation with the empty boron π orbitals are predicted to be roughly electroneutral (i.e., occupied by one or slightly less electrons), whereas in a similarly parametrized calculation for ethane these orbitals are found to contain ~0.08 excess electron. One concludes then that donation to the boron π orbital is mainly from the carbon quasi-π orbital which was electron rich by virtue of natural, unperturbed acceptance from hydrogen. On the other hand, boron returns a considerably greater fraction of an electron through the σ-orbital framework than it accepts through the π-framework. (The quasi-π orbital of carbon not capable of conjugation is little affected, having 0.05 excess electron per carbon.) Therefore, not only are the carbon atoms made electron rich by 0.2—0.3 compared to those in ethane, but even their hydrogens are on the average 0.01 less electron deficient than they are in C_2H_6.

Upon examination of the boron and its substituent methyl groups in the adduct, several very important differences in charge distribution may easily be discerned. The $2p_z$ boron orbital (formerly $2p\pi$ in the reactant) now has $2/3-3/4$ of an electron, most of which has been donated by nitrogen. The large over-all charge deficiency of boron, characterizing the reactant, is markedly decreased by the same mechanism. Interestingly, less of a decrease is noted in the anisotropic $2p\alpha$-calculation, mainly because of boron's smaller demand upon nitrogen and greater donation to its substituent methyl groups. The former results because the boron $2p_x$ and $2p_y$ demands which are weaker upon nitrogen under the second parametrization more than balance the stronger $2p_z$ demand which in any case gets a large fraction of the nitrogen $2p_z$-electrons, most of which belong to the lone pair *(vide infra)*. Similarly, decreased resistance to demand by methyl in the X- and Y-dimensions more than compensates for the reversal of demand in the Z-dimension. It should be noted that the pyramidal displacement of the methyls with respect to boron in the adduct mixes a small amount of $2p_z$ with $2p_x$ and $2p_y$ in the B–C bond directions.

Examination of the $2p_z$ orbital populations (q-values) for nitrogen in the uncomplexed amine and in the adduct indicates that $\sim 77\%$ of the lone pair is localized on nitrogen in the amine (in the HFMO, $q_{2s}=0.12$ and $q_{2p_z}=1.42$) and that most of the donation to boron is from this AO and hence from the lone pair. At the same time, all the other nitrogen orbitals which were in total ~ 0.25 electrons rich in the amine are only 0.08—0.12 electrons rich in the adduct. The amine alkyl groups have 0.04—0.05 in total more electrons in the adduct than in the reactant; therefore ~ 0.1 electrons from nitrogen *not from the lone pair* have been donated to the $-B(CH_3)_3$ fragment in the adduct. This fraction plus some of the lone pair donation may be considered as going to the boron methyls which are in total 1/3- to 1/2-electron richer in the adduct. The rest of the lone pair donation goes, of course, to decreasing the large boron deficiency which existed in the reactant but which has largely disappeared upon complexing. In total on the order of 3/4-electrons is transferred from $(CH_3)_3N$- to $-B(CH_3)_3$ and on the order of 3/5—3/4 of this can be construed in terms of lone pair sharing in the adduct.

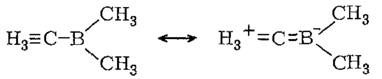
A further word concerning delocalization of the lone pair in the uncomplexed amine is in order. Roughly 23% delocalization is predicted, compared to only 4% for NH_3 and 14% for HCN from SCF calculations [1], which seems intuitively a bit high. Much of this effect is however doubtlessly due to the comparatively large of the molecule which spreads charge out over many of the filled MO besides the HFMO. Moreover, charge leakage onto methyl through the non-planar σ-framework is possible. Less easily rationalized is the very small $2s-2p$ mixing in the lone pair on nitrogen, i.e., $1:12$ vs. $1:8$ in NH_3 [1], with similar $\sphericalangle RNR = 108^\circ$. This may be the consequence of relatively strong involvement of the N 2*s* with C2*s* in the σ-framework, an interaction whose ramifications are further examined below.

The hydrogen charges are of considerable interest as well. In the comparable ethane calculation, the hydrogens are found to each be 0.11 electrons deficient, about the same or perhaps just slightly more than they are in the uncomplexed trimethylboron. From our previous analysis we concluded much of the π-electron donation to boron originated from the hydrogens although considerable return from the former to the latter through the σ-framework was noted. In the adduct, where the previously formally empty orbital of boron is filled by nitrogen, the boron demand upon the electron reservoir of its alkyl substituents is decreased and the charge deficiency of its hydrogens decreases, less however in magnitude than the change which occurs at the carbons ($\sim 1/5$ on a per atom basis). By the same token, the relatively minor charge deficiency on hydrogen in the uncomplexed amine is increased upon complex formation; all of the charge flow however may be considered to go to the carbons binding these hydrogens, which in the process of addition have become significantly more electron rich. The latter effect, that is, pile up of electrons on the carbons while the atom to which they are formally bonded is being strongly drained, constitutes the most puzzling result yet discussed when viewed from an empiricists position. Further details related to this phenomenon are considered below.

3. Atom and Orbital Overlap Populations

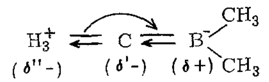
The picture of electron flow accompanying complexation which begins to emerge from consideration of atom and orbital charge populations (charge densities) is given added detail by examination of the overlap populations which are in essence bond order measures. Tables 3 and 4 reveal the formation of a B–N bond with total OP of 0.69, comparable to the value for the C–C bond in ethane of 0.79 considering the interatomic distance difference. The $p\sigma$–$p\sigma$ component (0.30) is in fact somewhat more important than in ethane (0.31) when this distance difference is considered, again indicating the validity of intuition when assigning major importance in binding to the nitrogen lone pair. The B–N and C–C pairs, constituting isoelectronic diatomic fragments, may be further compared with respect to their quasi-π interactions. They are likewise similar; both are normal in the sense of demonstrating small negative OP's as is usually found for quasi-π populations between "saturated" atoms. The smaller negative populations observed in the B–N bond (for ethane the two orthogonal quasi-π OP's are each -0.025) is mainly due to its greater bond length. For comparison, in the adduct with central bond length 1.80 Å, the total OP is 0.635, the $p\sigma - p\sigma$ component is 0.291 and the two quasi-π populations are $+0.001$.

The preceding outlines the most important details of the only new bond formed upon complexing. Changes in the OP's of bonds already extant in the reactants are also of much and perhaps even greater importance with respect to the earlier posed questions. With the intuitive expectation that the π-quasi-π bonds between the heteroatoms and their respective methyl carbons should undergo the most profound OP change during reaction, we may proceed to examine the results for each molecule in detail. In $B(CH_3)_3$, the π-quasi-π OP of 0.08—0.11 suggests considerable π-bonding, consistent with the earlier charge density results which suggested electron flow in the π-framework to the formally empty boron orbital. The rudimentary valence bond representation of dative HCJ interaction,



,

is substantially supported. When one adds to this picture in terms of what has already been discussed a more appropriate representation is forthcoming.

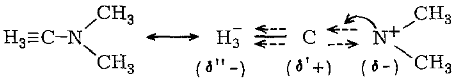


Here the inductive shift ($\sigma - \sigma$ and quasi-π-quasi-π) is described by the arrows and the resultant charge distribution, normalized to ethane, by parentheses (with $\delta \gg \delta' > \delta''$). These results strongly substantiate Mulliken's intuitive MO and reactivity correlation analysis of stabilization effects in $(CH_3)_3B$, contrasted with borane, BH_3, where dative HCJ is not possible [13].

Considering the alkyl boron as part of the adduct, both the carbon-boron π-interactions become quasi-π-quasi-π and are both characterized by negative OP's. The total C–B population decreases approximately by the difference between the π-quasi-π value in the reactant and the quasi-π-quasi-π value in the adduct. Clearly, then, what have been accepted as important dative HCJ effectes present in the uncomplexed alkylboron are not present in the adduct.

This view is further supported by a detailed consideration of the carbon hydrogen bond OP's in the boron methyls. The low average total CH population in the reactant (compare with 0.758 in ethane) is increased in the adduct to very near a normal (ethane) value. Most of the deficiency in the former may be attributed to the weakness of the bond between the formally conjugating carbon π orbital ($2p_z$) and the hydrogen most favorably disposed for overlap with it, consistent with the VB structure drawn. The notation used for this interaction is $p\pi H$ although it is to be recognized correctly as a $2p\sigma C - 1sH$ interaction component for the individual hydrogen perpendicular to the BC axis. Further support for the VB structures is to be found from the $p\sigma H$ values (component along the B–C axis); this actually decreases upon complexation indicating the electron return along the σ-framework from boron to carbon and hence to hydrogen, significant in the reactant, is diminished. The difference in total C–H OP's noted between the calculations using the two parameter sets, sizable only for the alkylboron molecule, is due overwhelmingly to the difference in the $2p_z$ electronegativities and is mainly reflected in the $p\pi H$ value. The latter is even smaller in the anisotropic $2p\alpha$ calculation than the small value shown in Table 3 (compare with 0.514 in ethane); a difference between parameter sets paralleling in magnitude, but quite reasonably opposite in direction to, the difference noted for the B–C π–π populations. In agreement with the earlier findings concerning charge density, all the components of the boron methyl C–H overlap population approach ethane-like values in the adduct.

The amine methyl C–H OP's, while not changing as dramatically upon complexation, deserve some attention. These values are low compared to ethane principally because of diminished $2s$C–$1s$H contributions, apparently due to the electron withdrawal occasioned by the large nitrogen-carbon $2s\alpha$ difference. This and previous information suggest the following VB picture for the free amine.



Here the lower dotted arrows indicate a bond weakening (OP decrease), with donation in the directions noted, of the C–N and less dramatically of the C–H σ-bonds ($\delta' > \delta > \delta''$) with return from nitrogen via the π-framework, much of which ends up on hydrogen. It should be noted that these conclusions are in part made on balance since, unlike alkylboron, the amine is not planar and the consequent mixing of orbitals inevitably complicates the meaning of such quantities as $p\pi\pi$ and $p\pi$H. Even so, this VB picture seems consistent with all the results for the amine from Table 3 and seems capable of substantially accommodating the amine in complex as well. In the latter the small positive N–C component-π-quasi-π OP ($\sim$0.01) present in the amine has disappeared ($<$0.0002) because of utilization of the nitrogen lone pair in the σ-bond made to boron. Concomitantly, the electron distribution measures of the amine methyl groups move in the direction of, but do not reach normalcy (in the ethane sense), consistent with decreased lone pair delocalization into these groups. Charge buildup on the methyl carbons, viewed as enigmatic previously is satisfactorily accommodated in this representation. The C–H overlap populations are predicted to be considerably less sensitive to complexing than are the charges; this is not surprising when the relative importance of the $2s$ orbitals and small changes in geometry in the amine with reaction are recalled. The average of these CH bond orders are, in fact, predicted to remain essentially constant between reactant and product, in sharp contrast to the behavior predicted for the boron methyls. This shall be a most relevant difference in the comparisons with, and interpretation of various experimental data for the equilibrium system now to be discussed.

Derivative Theory and Comparisons with Experiment

1. Isotope Effects upon Position of Equilibrium

What is doubtlessly the most precise experimental examination of the reaction system of interest to date, and at the same time most pertinent to the results discussed here was carried out by Love et al. [14] and concerns the effect of perdeuteration in the alkyl boron on the position of equilibrium in the gas phase. These workers employing a modification of a manometric procedure developed by Brown [12] found a K_D/K_H ratio (equilibrium constants for association) of 1.25 ± 0.03, fairly well temperature independent over the range 65—95° C. Qualitative theory would have anticipated the direction and not have been in conflict with the magnitude of this result from analogy with organic reactions where carbonium ions are intermediates in neutral molecule decompositions. In the latter, k_D/k_H (rate) ratios less than unity are found and interpreted in terms of HCJ stabilization of the transition state but not of the reactant state, with deuterium substitution favoring the state having the strongest C–H binding. In the present case, this stabilization is exercised the other way around (in the reactant and not in the product), with lesser relative C–H bond strength changes expected than in the ion-forming reactions. The theoretical results obtained here are entirely consistent with these arguments and, excluding the temperature effects upon which they cannot be brought to bear, with the experimental results as well, a consistency which persists when extensions to quantitative comparisons are attempted.

It may be shown by a method developed for carbonium ion- and radical-forming reactions that kinetic β-deuterium isotope effects can be directly correlated with the changes in average C–H overlap population predicted to accompany reaction [15]. The method relies upon the finding that a linear C–H bond length-OP relation exists, obtained from consideration of several small molecules whose geometries are known precisely. (Ethane, ethylene and acethylene yield an excellent linear relation in these measures.) From this relation and the computed CH OP's in the molecule of interest, the CH bond length change expected to occur upon reaction may be obtained, generally by extrapolation on the known molecule line. From this average bond length change and employment of a force constant-bond length relationship such as Badgers rule, the change in CH force constants with reaction is estimated. This apparently indirect method may be shown to be more reliable than approaches based on direct estimation of molecular energy as a function of bond distortion. The latter are known often to yield incorrect behavior even where application of rigorous methods with limited basis sets are made (e.g., displaced minima, incorrect curvature), in the regions near the correct internuclear separation.

Under the assumption that stretching contributions are energetically more important than bending contributions (i.e., $\Delta k_S \gg \Delta k_B$), perturbation theory yields the following reaction energy relationship.

$$\delta(\Delta E) = \frac{1}{2} \Delta k \cdot \delta\overline{(r-r_0)^2}\,. \tag{3}$$

Here Δ indicates the change accompanying reaction: ΔE is the electronic energy change and Δk is the change in CH stretching force constant. On the other hand, δ indicates change due to isotopic substitution: $\delta(\Delta E)$ is the difference in electronic energy change accompanying reaction between the protium and deuterium substituted systems and $\delta\overline{(r-r_0)^2}$ is the difference in the mean of the displacement squared of coordinates involving methyl hydrogen motion. [It is interesting to note that anharmonicity effects allowed for by the theory, i.e., in $\overline{(r-r_0)}$ terms, are cancelled in the final expression, Eq. (3). Details of the development of this equation will be described elsewhere.]

From these relationships the boron methyl CH bonds are predicted to shorten by 9×10^{-4} Å going from reactant to adduct, compared to a lengthening of 3×10^{-3} Å for the comparable bonds in the reaction process, t–BuX → t–Bu$^+$ + X$^-$. Note, the t-butyl cation is isoelectronic with $B(CH_3)_3$. The force constant changes which pertain are 0.14 mdyne/Å for the addition versus -0.46 mdyne/Å for the S_{N1}-type decomposition. The 0.14 mdyne/Å value may be checked against that obtainable from the experimentally measured C–H stretching frequency change [16] (2941 cm^{-1} in the uncomplexed alkylboron and 2870 cm^{-1} in the adduct) using a diatomic molecule average frequency approximation [17], $v^2 = (2\pi c)^{-2} \cdot k(\mu_H + \mu_X)$, where the μ's are reciprocal masses. The value for Δk obtained this way is 0.12 mdyne/Å. Employing a $\delta\overline{(r-r_0)^2}$ value of 1.72×10^{-3} Å^2 (H − D) obtained from a study on deuterated methanes [18], and verified to be of fairly general validity for other molecules [15], an isotope effect K_D/K_H of 1.03 *per D* is computed, compared to 1.10 per D in the opposite direction for the *t*-butyl decomposition. The predicted K_D/K_H value for perdeuteration relative to the normal system is then 1.30, certainly in excellent agreement with the observed results, especially in light of the mentioned and such implied approximations as the zero-point energy approximation (which would, incidentally, suggest T^{-1} dependence of the K-ratio) and the neglect of bending force constant and charge redistribution effects.

The predicted smaller isotope effect in the boron than *t*-butyl system is in agreement with experiment; effects of 10—20% per D have been observed in S_{N1} reactions [19]. The danger of attempting quantitative judgements on the basis of comparison among isoelectronic systems is again demonstrated as it has often been when quantitative results became available. Theory clearly anticipates the difference on the basis of orbital exponent differences; under no circumstances of approximation would the electron demand of the p_z, and subsequent donor properties of the $p\sigma$ orbitals of boron apply to the formally positively charged carbon in the ion.

2. Further Experimental Comparisons and Suggestions for Additional Inquiries

Several other pieces of experimental data have been obtained for this reaction system and its individual components. The pure quadrupole resonance spectra of trimethyl- and other alkylborons have been measured [20] and found to correlate with effects predicted by classical charge flow notions. Upon successive symmetrical trialkyl substitution of the higher and branched members, the $B^{11}\, e^2Qq$ values were found to increase in a manner consistent with successive decreases in electron density in the p_z or formally empty boron orbital. This is qualitatively in accord with the decrease in number of alkyl hydrogens capable of HCJ interaction with the B $2p_z$ orbital.

If sp^3-sp^3 C–C bonds are granted the capability of hyperconjugation, as theory and linear free energy correlations seem to suggest ($h_C/h_H = 2/3 - 3/4$, denoting effects on charge delocalizability as well as on stabilization energy [21]), and free rotation of the alkyl groups is assumed, a semi-quantitative and reasonably internally consistent estimation of the average electron density in the p_z orbital ($\bar{q}_z$) can be obtained from the e^2Qq values for trimethyl-, triethyl- and triisopropylboron. The values reported in Ref. 20, respectively 4.876, 5.003 and 5.250 Mc/sec are adopted as is the following relationship between the quadrupole coupling constant and orbital charge density. It is of interest that all other straight chain alkyl groups yield e^2Qq values within 0.0003 that of ethyl.

$$e^2Qq_{zz} = k\left[\frac{1}{2}(\bar{q}_x + \bar{q}_y) - \bar{q}_z\right]. \tag{4}$$

Here, k, which is a function of the electrostatic field gradient along the Z-axis should be roughly constant under the present substitutions. The ratio of e^2Qq-values will then be, assuming $\bar{q}_x$ and $\bar{q}_y$ experience the same inductive effects and

C–H and C–C bond effects are additive with $h_C/h_H = 2/3$,

$$e^2Qq_{zz}[(CH_3)_3]/e^2Qq_{zz}[(CH_{3-n}Me_n)_3] = \left[\frac{1}{2}(\bar{q}_x+\bar{q}_y)-\bar{q}_z^{TM}\right]\bigg/\left[\frac{1}{2}(\bar{q}_x+\bar{q}_y)-\left(\frac{3-n}{3}+\frac{2}{3}\,\frac{n}{3}\right)\bar{q}_z^{TM}\right]. \tag{5}$$

The $\bar{q}_z$ value for the trimethylboron ($\bar{q}_z^{TM}$) is predicted to be 1/8 or 1/5 electron, depending upon whether the $\bar{q}_x$ and $\bar{q}_y$ values of Table 3 are used or whether the zeroth-order approximation is made that one electron occupies each of these σ-orbitals. The difference is mainly in this scaling; comparisons among the alkyl substituents taken in pairs is much more consistent. With h_C/h_H equal 3/4, the comparable $\bar{q}_z^{TM}$ values are $1/6-1/4$ electron. Table 3 on the other hand predicts $\sim 1/3$ electron is donated to this orbital by the methyls. In the highest filled MO of $(CH_3)_3B$ having appreciable p_z density, ~ 0.1 electrons are predicted to be found in the $2p_z$ orbital. It may be further noted that deuterium substitution in $(CH_3)_3B$ also causes quadrupole coupling shifts consistent with the HCJ interactions discussed. The CD_3 group, less capable than CH_3 in delocalizing electrons to boron, should produce a slightly higher coupling constant for the boron. The effect observed in B^{11} is ~ 30 kc/sec [20]. Additional evidence of a physical (generally spectroscopic) nature to support the conclusion of π-delocalization involving boron in systems where it bears organic group substituents are reviewed in Refs. 20 and 22.

The early data of Brown [12] where successive substitution of methyl groups for hydrogen in the amine was found to produce a non-monotonic ordering of basicities with respect to $B(CH_3)_3$ is pertinent in a chemical reactivity sense. The levelling of increased basicity noted for substitution of a second compared to the first methyl, and inversion of effect upon substitution of the third, led Brown to postulate his B- (as opposed to F-) strain hypothesis of steric effects. Support for this being in the main a nitrogen configuration problem is, it is claimed, indicated by a similar basicity order found for proton addition [12, 23]. This appears to be an attractive hypothesis, yet the direct evidence advanced in its support is not satisfying. Outside of the proton addition results, the major arguments are structural in nature, i.e., that the multiply methyl substituted amines already evidence strain indicated in their bond angles which should be increased in going to the adduct. However upon examination of structures one finds the CNC angles in the di- and trimethyl amine to be identical and further no evidence that these angles are substantially different from tetrahedral. In $(CH_3)_2NH$ this angle is $108 \pm 4°$ or $111 \pm 3°$ from two determinations and for $(CH_3)_3N$, $108 \pm 4°$ all from Ref. 6, but more recently $108°41' \pm 1°$ for the latter [24], certainly casting doubt on the notation of strain in the uncomplexed amine (NH_3 has angles of 108°48′). There is of course no reason to assume that the adduct, even if it were B-unstrained would exhibit tetrahedral CNC angles as Brown implies, since the fourth group, the $B(CH_3)_3$, is quite different from the other three on nitrogen. Viz., the CNC angle in $(CH_3)_3NBF_3$ is 114° with $r_{NB} = 1.585$ Å [9], although one must grant that different repulsion situations exist, which are, incidentally, F- and not B-strain dependent. On the other hand, the compromise structure accepted here has CNC angles of 105.5°.

Further support for the Brown hypothesis, beyond this unconvincing collection of structural facts, might however be obtained by examining the effect of deuteration of the amine methyl groups on the position of equilibrium for complexing. An increase would be expected. This would be an interesting experiment to perform; the results of Table 3 and 4 indicate no electronic effects in either the usual sense or to the extent which steric repulsions are recognized. I.e., there is essentially no OP change in the CH bonds and hence no zero-point energy dependent isotope effect predicted for this reaction. Precise redetermination of the structure of the adduct is of course desirable with regard to interpretation of this and all other electronic effects operative in this system.

Conclusions

To the extent that a theory such as is presently used and parametrization procedures which depend upon the results for rigorously treated similar but by no means identical molecules are valid, the molecular orbital results presented and discussed above must be judged as generally confirming previous qualitative notions concerning electronic interactions in the trimethylboron-trimethylamine addition system. Arguments presented concerning the extra stability of trialkylated boron, compared to borane, due to dative hyperconjugative effects appear sound. That profound σ-framework polarization in the direction opposed to π-donation to the boron should occur in $(CH_3)_3B$, and that formation of the adduct should occur upon donation of the nitrogen lone pair to boron, with relaxation in the electron demand by nitrogen upon its substituent methyl groups, are also borne out by these calculations.

Besides adding a quantitative aspect to these details of electron distributions, combination of the MO and perturbation theories allows estimation of the deuterium isotope effects upon position of reaction equilibrium. Substitution of deuterium for hydrogen in the boron methyls is predicted to increase the equilibrium constant for adduct formation by $\sim 3\%$ per deuterium (in good agreement with experiment), and to have essentially no effect when the substitution is in the amine methyls (not known experimentally). The latter are zero-point electronic energy estimations and do not comprehensively cover steric retardation arguments. The effects of such (Brown's B- and F-strain) on isotope effects and upon the geometries of reactants and product have also been considered subsidiarily in a qualitative fashion. Other pertinent experimental data such as quadrupole coupling constants in alkyl borons have been examined and found to be consistent as far as their analysis and the present results may be collated with the picture of electronic distributions obtained.

Attention has been drawn explicitly to differences in environment for certain of the atoms here compared to the molecules from which their parameter values were obtained. This is especially true of boron. How these differences are expected to affect the individual molecule as well as equilibrium properties of the addition system of present concern, and possible generalizations to other systems are examined in the accompanying paper.

The author wishes to acknowledge several useful discussions of this and related work with Max Wolfsberg.

References

1. Newton, M. D., F. P. Boer, and W. N. Lipscomb: J. Am. chem. Soc. **88**, 2353 (1966), and following papers.
2. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
3. Mulliken, R. S.: J. Chim. physique **46**, 497, 675 (1949); J. physic. Chem. **56**, 295 (1952).
4. Wolfsberg, M., and L. Helmholtz: J. chem. Physics **20**, 837 (1952).
5. Hoffmann, R., and W. N. Lipscomb: J. chem. Physics **36**, 2179 (1962) and later papers, many in the same journal.
6. Tables of Interatomic Distances and Configurations in Molecules and Ions, Scientific Editor, L. E. Sutton, The Chemical Society, London 1958.
7. Lide, jr., D. R., R. W. Taft, jr., and P. Love: J. chem. Physics **31**, 561 (1959).
8. — J. chem. Physics **32**, 1570 (1960).
9. Geller, S.: J. chem. Physics **32**, 1569 (1960).
10. Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
11. Mulliken, R. S.: J. chem. Physics **23**, 1833 (1955), and later papers in the same volume.
12. Brown, H. C., H. Bartholomay, and M. D. Taylor: J. Am. chem. Soc. **66**, 435 (1944).
13. Mulliken, R. S.: Tetrahedron **5**, 253 (1959).
14. Love, P., R. W. Taft, jr., and T. Wartik: Tetrahedron **5**, 116 (1959).
15. Ehrenson, S., and M. Wolfsberg: Unpublished results.
16. Love, P.: Ph. D. Thesis, The Pennsylvania State University, 1961.
17. Cf. Bernstein, H. J.: Spectrochim. Acta **18**, 161 (1962).
18. Kuchitsu, K., and L. S. Bartell: J. chem. Physics **36**, 2470 (1962).
19. Cf. Halevi, E. A.: Secondary Isotope Effects, Progress in Physical Organic Chemistry, S. Cohen et al., eds., Interscience Publishers, New York, N.Y., Vol. I, 1963; K. T. Leffek, A. Queen, and R. E. Robertson, J. Am. chem. Soc. **87**, 161 (1965).
20. Love, P.: J. chem. Physics **39**, 3044 (1963).
21. Taft, jr., R. W., and I. C. Lewis: Tetrahedron **5**, 210 (1959); R. W. Taft, jr., and M. M. Kreevoy: J. Am. chem. Soc. **79**, 4011 (1957); S. Ehrenson: J. Am. chem. Soc. **86**, 847 (1964).
22. Coyle, T. D., and F. G. A. Stone: J. Am. chem. Soc. **82**, 6223 (1960) and other references cited therein.
23. Brown, H. C.: J. Am. chem. Soc. **67**, 374 (1945).
24. Lide, jr., D. R., and D. E. Mann: J. chem. Physics **28**, 572 (1958).

Dr. S. Ehrenson
Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973, USA