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Environmental Effects in the MO Treatment of the Trimethylamine-Trimethylboron Addition Reaction*

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An attempt has been made to estimate charge redistribution effects in the Lipscomb MO treatment of the trimethylamine-trimethylboron addition reaction. The zeroth-order results which show substantial electron shifts and features suggesting charge imbalance in the amine and alkylboron accompanying reaction are modified by a self-consistent, linear α-upon-orbital charge adjustment method. The form and parametrization are derived from known atom behavior upon charging and from attempts at separation of charge effects in limited SCF calculations for simpler molecules. Whereas the charge imbalances appear to be satisfactorily remedied, the method as presently parametrized does not simultaneously improve correlations with the limited set of experimental observables for this reaction system.

Ein Versuch zur Abschätzung der Ladungsumverteilung bei der Dimethylamin-Trimethylboran Addition wurde mittels des MO-Verfahrens nach Lipscomb gemacht. Die Ergebnisse der nullten Ordnung, die wesentliche Elektronenverschiebungen zeigen und darauf hindeuten, daß die Reaktion zu unwahrscheinlichen Ladungsverteilungen im Amin und Alkylboran führt, werden durch eine lineare Beziehung zwischen α und der Orbitalladung modifiziert. Form und Parameter erhält man aus dem Verhalten von Atomen gegenüber Zusatzladungen und aus Separationsversuchen von Ladungseffekten bei einfachen SCF-Rechnungen an kleineren Molekülen. Zwar verschwindet die problematische Ladungsverteilung, aber der Grad der Übereinstimmung mit einigen anderen experimentell beobachteten Größen bleibt bei den gegenwärtigen Parametern unverändert.

On a tenté l'estimation des effets de redistribution de charge dans le traitement O. M. de Lipscomb pour la réaction d'addition triméthylamine-triméthylbore. Les résultats d'ordre zéro qui révèlent des déplacements électroniques importants et suggèrent le non équilibre des charges sont modifiés par une méthode self-consistante d'ajustement linéaire des charges. La forme et les paramètres sont déduits de la connaissance du comportement atomique à la charge et de tentatives pour séparer les effets de charge dans des calculs SCF limités pour des molécules plus simples. Alors que les déséquilibres de charge sont compensés d'une manière satisfaisante, la méthode ainsi paramétrisée ne premet pas d'améliorer simultanément les corrélations avec l'ensemble limité d'observables expérimentales du système réagisant.

Introduction

In the preceding paper [1], application of the Lipscomb MO method [2] to the trimethylboron-trimethylamine reaction system was found to yield results which were generally consistent with experiment where comparison was possible. These results also agreed in most details with previous qualitative theoretical estimations of effects operative in the individual molecules. Most striking in this regard was the confirmation of strong dative hyperconjugative (HCJ) stabilization in the free alkylboron and its subsequent disappearance in the adduct, a change which was shown to account for the observed boron methyl deuterium isotope effect.

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At the same time, it became apparent from some fairly limited computational comparisons that quantitative estimations of various theoretical quantities such as charge densities and bond orders showed non-negligible dependence upon the parameters employed in the method, and further that some of the changes in these quantities accompanying reaction were neither intuitively obvious nor satisfactorily justifiable on appeal to the precepts of more rigorous theory. An example of the former was to be found in the boron π-orbital charge density value, $q_{B\pi}$, which, although not affecting the conclusion of strong π-acceptance by boron in $(CH_3)_3B$, varied significantly between the two calculations described. The result that the amine methyl carbons become more electron rich in the adduct was empirically disquieting. Continued increase in the absolute magnitude of the total orbital electronic energy as the B–N bond is stretched from 1.65 to 1.80 Å *and beyond*, and the inability to obtain CH stretching force constants from the variation of computed energy with bond distortion illustrate the latter and certainly indicate fundamental variance from rigorous SCF theory.

It is to an examination of these points that the present paper is devoted. The results obtained on the trimethylboron-trimethylamine are especially pertinent since this system represents not only one of great chemical interest but one in which fairly profound differences in atom environment accompanying reaction are to be expected. (It is doubtlessly because of these internal environmental differences that the system shows appreciable and therefore interesting chemical reactivity effects – complicating effects such as are often encountered in other interesting reactions, e.g., those of solvation and the effects of counterions where formal ion charges exit, are absent here.) On the other hand, the theory is sufficiently closely related to rigorous theory so that departures from well defined points may be recognized. That is, the environmental change for an atom in either reaction state may be referred to that for the atom as it exists in the basis molecule, from whence the original parametrization was obtained. The distinction from more empirically based theory is important. The fundamental questions which pertain are, which of the original parameter set are satisfactory for general needs as the atoms are transferred from one to another, not necessarily very similar molecule, and is there some way of anticipating the correct change, or correcting *in situ*, for those which must change as the environment is varied.

Applications and Extensions of the Theory

It is apparent from examination of the Lipscomb theory that the major deficiencies which limit its widespread use are the obscurity, in the direct (experimental or empirical) sense, of the origins of the diagonal matrix elements ($F_{ii} = \alpha_{ii}$) and how these are expected to change with variation in molecular environment. Reiterating the basic equations,

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

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

This is not to say that knowledge of the origins of these terms is unavailable; recourse to the correct SCF Hamiltonian and limited SCF wavefunction are not however to be suggested if the method is to be of general utility for chemically interesting molecules. These diagonal matrix elements are extracted from limited

SCF calculations and confidently may be applied therefore only in the molecules from which they are derived or in closely related ones. At least two important variations must be recognized and hopefully accounted for upon departure from the equilibrium configurations of the basis or standard molecules. The first concerns a structural variation; that is, what happens upon the stretching or bending of bonds? The second recognizes a more profound change. What happens when the atom of interest is placed in surroundings with ligands which make different electronic demands than were present in the basis molecule?

That the F_{ii} and F_{jj} elements, at the very least, must change upon distortion of the bond between atoms i and j in a polyatomic molecule is evident from the failure of the method to reproduce anything like correct equilibrium geometries. This failure has been mentioned above and commented upon in the original references [2]. Subsequent work has established the kinetic energy terms as major contributors to this failure, at least in the empirical sense [3]; poorer potential energy *versus* bond distance behavior is generally noted than in the earlier valence state ionization potential methods [4]. The fault is in actuality not due to the kinetic energy adjustments, which are made explicitly and rigorously, but rather that in a method which attempts to parametrize together proper one-center and such two-center interactions as are expressed by Coulombic and electron repulsion terms, technique improvement (i.e., separation of potential and kinetic energy terms in the Hamiltonian matrix to effect more consistent two-center matrix element computation) does not necessarily produce uniformly better results for all molecular properties.

The possibility should not be discounted that the diagonal matrix elements or α's not directly involved in the distorted bond may also vary non-negligibly. In fact, of all the terms from which the matrix elements are constructed, confidence in the invariability of only one set, the K_{ij}'s, seems warranted. That these quantities would not change substantially is suggested by their demonstrated insensitivity to much greater physical variations, i.e., changes in surroundings and in the nature of the atoms i and j themselves.

Charge distortions accompanying environment changes must have similar profound effects on the F_{ii} terms. (Henceforth the terms charge, net charge and population will be used interchangeably.) Lipscomb et al. [2] in consideration of methods to account for these intramolecular effects have lumped both types of distortions together. From plots of SCF α values *versus* atom populations (charge densities), Figs. 1 to 3 of Ref. 2, number I, where no distinctions are drawn concerning hybridization, type, number and nearness of neighboring atoms, they conclude a linear relationship does not exist. The entire question is dropped at this point after citation of earlier work by Mulliken suggesting that significant and variable interplay among these factors must exist [5].

An attempt to separate these factors may be made. If in the plots just mentioned, restrictions to the grouping of similar molecules only are made, e.g., hydrocarbons considered by themselves for the carbon and hydrogen dependencies, fairly good linear correlations may be obtained. (For the former, separation into $2p\sigma$, $2p\pi$ and $2p\pi_{\text{quasi}}$ sets show such correlation better than their averages.) The values of $\Delta\alpha/\Delta q$ obtained are, in units of eV/electron, H1s, -15, C2s, -4, and for the average of the C2p slopes, -11. The Δq values are net atomic charges. Unfortunately, all the boron and nitrogen containing molecules examined are quite different; hence, a similar analysis is not possible.

While these values arise from groupings intended to minimize neighboring heteroatom effects, the number of nearest (similar) neighbors and how close they are still are variable. An alternative way exists however to estimate $\Delta\alpha/\Delta q$ which removes all these factors. If one fits the known valence state energies for the neutral and $+1$ and -1 charged atoms to a quadratic form in charge, to the extent that these energy differences reflect the change in the orbital α-terms and are transferrable to molecules containing such atoms, the following holds:

$$\alpha' - \alpha = [M + N(q' + q)]\,(q' - q)\,, \tag{3}$$

where,

$$M = [A(q_v^+ + q_v^0) - I(q_v^- + q_v^0)]/(q_v^- + q_v^+)\,, \tag{4}$$

$$N = [I - A]/(q_v^- - q_v^+)\,. \tag{5}$$

The v-subscripts on the q's indicate valence state charge densities for the atom and the unsubscripted quantities in Eq. (3) pertain to the orbitals of this atom in the molecule. Note that the valence state ionization potentials, I, and electron affinities, A, allow analysis in orbital charge density terms.

Where q_v^+, q_v^0 and q_v^- are, as usual, 0, 1 and 2 and where Δq (i.e., $q' - q$) is small in Eq. (3), a quasi-linear form can be realized,

$$\Delta\alpha = -\left[\frac{3I - A}{2} + (A - I)q\right]\Delta q\,. \tag{6}$$

For $q = 1$, the parenthesized quantity becomes $(I + A)/2$, the familiar Mulliken electronegativity measure, χ_M [3]. When q differs from unity, as it may in molecules, this coefficient is often quite different from χ_M. For C2s where q is generally ~ 1.25 [2], this quantity turns out to be ~ 12 eV/electron, compared to χ_M of 15 eV/electron. For the C2p's where q is typically 0.9 to 1.1, values ± 1 eV of χ_M (5.8) are encountered. For H1s, with q's in the range 0.8–0.9 in hydrocarbon molecules, the parenthesized quantity is 1.3–2.7 eV higher than the χ_M value of 7.2. All values have been computed with I and A values taken from the recent compilation of Hinze and Jaffé [6].

It is interesting to note that these coefficients, which represent the α-upon-charge density dependence of the atom as it might be expected to behave in the molecule (neglecting at least to the first order the anisotropies due to neighboring atoms), are generally closer to the values obtained from the SCF-α *vs.* q plots than are the corresponding χ_M values. The valence state I and A method developed, it should also be noted, yields identical results for Δq considered in orbital or net atom charge terms since the atom is treated in isolation. This is not true for the more empirical molecular relationship described previously. There, plotting α against orbital charge generally yields considerably poorer correlations, mainly because the anisotropies introduced by variable numbers of substituents, differently arranged, quite reasonably have stronger effects on the spatial charge distribution than on its average over the whole atom. Even so, some rough values may be abstracted for the α-upon-orbital charge dependence assuming this dependence to be linear. For H1s the value is of course the same as previously given (-15 eV). For C2s in the hydrocarbons the value is -0.5 ± 0.2 a.u. or ~ -11 eV. For the

C2p, the only orbital exhibiting a sizable slope is $2p\sigma$, a similar situation as was encountered when Δq was taken as the net atomic charge difference. The changes in q for these orbitals are so disproportionately small however over the series of hydrocarbons for which data is available (CH_4, C_2H_6, C_2H_4 and C_2H_2) that one can only conclude that the average slope should be somewhat larger than the value of -11 eV/electron previously obtained.

From the preceding admittedly rough and limited comparisons it seems fair to conclude that the variation of α with q expressed in Eq. (6) with typical orbital charges approximates the behavior obtained from the hydrocarbon molecule plots as closely as one could expect considering the effects neglected. To bracket these hydrocarbon values, χ_M, on the one side, with greater variation among the orbitals than is obtained from Eq. (6), and the measure $I-A$, on the other, which levels the difference between orbitals, will both be employed to determine the effects of charge redistribution in the CH parts of the reaction system of interest. The quantity $I-A$ which is a measure of self-charging, i.e., for the process $2X \rightarrow X^+ + X^-$, together with $(I+A)/2$, which is the average energy of ionization from the neutral and negative ion states of X (that is, for $X + X^- \rightarrow X^+ + X$), in fact bound the Eq. (6) values of all orbitals of concern with the exception of N2p. Therefore, the $I-A$ and χ_M bounds are used for all orbitals except N2p; for the latter, the Eq. (6) value, -5.1 eV/electron, is used instead of $I-A$. The boundary values of these slopes, ω's, are shown in Table 1.

Table 1. *Zeroth-order MO and charge redistribution parameters*[a]

Orbital	Exponent	α^0	q^0	$\omega(\chi_M)$	$\omega(I-A)$
B1s	4.700	-7.706	(5.283)[e]	0.0	0.0
2s	1.300	-1.081	1.025	0.378	0.338
$2p_{x,y}$	1.300	-0.337[b]	0.754	0.161	0.298
		-0.286[c]	0.768		
$2p_z$	1.300	-0.337[b]	0.754	0.161	0.298
		-0.439[c]	0.727		
C1s	5.700	-11.284	(6.372)[e]	0.0	0.0
2s	1.625	-1.449	1.248	0.550	0.445
2p	1.625	-0.364[b]	1.043	0.214	0.402
N1s	6.700	-15.519	(7.465)[e]	0.0	0.0
2s	1.950	-1.859	1.598	0.753	0.473
$2p_{x,y}$	1.950	-0.334[b]	1.287	0.312	0.187[f]
		-0.328[d]	1.056		
$2p_z$	1.950	-0.334[b]	1.287	0.312	0.187[f]
		-0.356[d]	1.760		
H1s	1.200	-0.537	0.860	0.264	0.472

[a] α-values in a.u., ω-values in a.u./electron. Valence state ionization potentials and electron affinities from Ref. [6]. [b] Averaged $2p\alpha$ and orbital population values from B_2H_6, C_2H_6 and NH_3 SCF calculations as recommended by Lipscomb et al., Ref. [2]. [c] $2p\alpha$ and populations by averaging of $2p_x$ and $2p_y$ from B_2H_6 SCF calculation. [d] From NH_3 SCF calculation. [e] Total electron densities from SCF calculations on B_2H_6, C_2H_6 and NH_3. [f] Value from the coefficient of Eq. 6 directly.

The form chosen for variation of α for the i-th orbital of atom k is,

$$\alpha_{ik} = \alpha_{ik}^0 + \omega_{ik}\{n(q_i^0 - q_i) + (1-n)(q_k^0 - q_k)\}, \tag{7}$$

in recognition of the influence of all orbitals of the atom upon the effective electronegativities of each other. The quantity n is a weighting factor to express this shielding; it has been arbitrarily taken as 1/2 with a single value of ω, making the effect upon α_{ik} of population density in orbital i twice as great as that of any other orbital on atom k. The arbitrariness of this choice and the bracketing procedure adopted suggests concern over a dual set of ω's (for orbital i *and* for the average over the other orbitals of atom k) to be unnecessary. The superscript zero refers to the terms obtained from the basis or standard molecule with which the zeroth order calculation is made. The form of Eq. (7) is seen to resemble that used in the conventional ω-technique as applied to simple Hückel theory [7, 8] where of course the second q-difference being assumed equal to the first removes the n-dependence. Several workers have recently made attempts to extend the ω-technique analysis in Hückel theory to include σ-framework effects [9] and for non-nearest charges [10] all with this form or ones derivable from Eq. (6). An interesting contrast may be drawn with Pople SCF theory where the diagonal Hamiltonian element has as important term the Mulliken electronegativity χ_M which is not however used explicitly as an adjustment variable in the SCF procedure [11].

Application of Eq. (7) to the overlap populations generates a new set of α's; upon cycling a self-consistent result may be obtained. That is, the α set employed in a given cycle will be consistent (to within a chosen limit) to the populations obtained from this cycle through Eq. (7), or the process is repeated until this condition is met. This procedure, akin to those generally employed in SCF calculations, is simply programmed as an addition to the routine described in Ref. [1]. Eq. (7), upon collection of terms is $\alpha_{ik} = A_{ik} + B_{ik}(q_i + q_k)$. The vectors A_{ik} and B_{ik} are input along with a threshold for convergence for the α's between successive cycles. Since the overlap matrix remains unchanged in this variation, its orthogonalization is unnecessary upon successive cycles after the first, reducing the self-consistency procedure to a repetitive matrix diagonalization and overlap population computation problem. To avoid the occasionally encountered problem of overshoot, a damping factor on the α-upon-q dependence was used which is mathematically justifiable, and here was taken to be 1/2. Extrapolation using a geometric mean procedure was also employed [8]. For all the calculations to be described, convergence was satisfactorily accomplished (to $<2\times10^{-3}$ a.u. in α for the reactants and $<1\times10^{-2}$ for the product) within 6 cycles.

Results and Discussion

Tables 2–4 contain digests of the most important results obtained for the trimethylamine-trimethylboron reaction system allowing for charge redistribution in the manner outlined. It should be reiterated at the outset of the discussion that the primary concern in this system is with the apparent charge imbalance which occurs upon complexation and what the redistribution scheme predicts on the basis of atomic and semi-empirical simple molecule behavior for amelioration of this imbalance. Geometric effects should be of lesser importance here and enter into our considerations only in the rehybridization of the boron atom upon reaction and to the extent they (geometry changes) complicate the empirical extraction of the α *versus* charge redistribution relationships. Hybridization changes are not a problem in the MO method employed as long as the mixing of orbitals is recognized and the proper quantities compared. The latter, i.e., mixing of effects upon α's, has of course been recognized in the preceding section and accounted for to the extent possible with the limited SCF data available.

In Table 2 the results using both alkylboron parameter sets of Ref. [1] as input are shown. The former which employs the same α-value for all $2p$ orbitals initially, maintains this isotropicity by averaging through all cycles. The latter, in which the $2p\alpha$ for the proper molecular π-orbital is distinguished from the others, has this distinction continued upon cycling. In general, the trends are found to be the same in both calculations. The $\omega(\chi_M)$ redistribution method changes the orbital electronic energy sum very little, in contrast to the $\omega(I-A)$ method. Both lower the energies of the HFMO (doubly degenerate) away from the observed IP value. These orbitals of e_x and e_y skeletal symmetry and characterized by major population density in the $p\sigma$ orbitals of boron and carbon are stabilized by the increased $2p_{x,y}$-α values on boron accompanying redistribution; explanations for discrepancies between the Koopman's Theorem ionization potentials and those experimentally observed have previously been cited [1, 2] and apply here as well.

Table 2. *Zeroth-order and self-consistent MO results for* $(CH_3)_3B$[a]

	Isotropic B2$p\alpha$[b]			Anisotropic B2$p\alpha$[c]		
Energies (a.u.)						
$-1/2\,\Sigma\,\varepsilon_i$	49.1478	49.1488	49.2008	49.1360	49.1288	49.1883
HFMO	−0.383	−0.398	−0.406	−0.368	−0.381	−0.390
Convergence[d]	–	6×10^{-4}(5)	5×10^{-4}(5)	–	6×10^{-4}(5)	4×10^{-4}(6)
Boron, net atomic and orbital charges, q						
$p_z(\pi)$	−0.348	−0.450	−0.518	−0.551	−0.667	−0.722
$2s$	0.255	0.037	0.090	0.249	0.048	0.096
p_x, p_y	0.397	0.327	0.295	0.463	0.398	0.368
Total	0.704	0.244	0.165	0.626	0.180	0.112
Methyl group charges, q						
C$p\pi$	0.000	0.010	0.025	0.039	0.056	0.070
C$2s$	−0.371	−0.287	−0.329	−0.387	−0.298	−0.340
C Total	−0.525	−0.381	−0.397	−0.532	−0.383	−0.399
Avg. H	0.097	0.100	0.114	0.101	0.108	0.120
Overlap populations, methyl carbon-boron, p						
π-quasi-π	0.076	0.087	0.092	0.094	0.100	0.102
quasi-π-quasi-π	−0.020	−0.022	−0.024	−0.019	−0.020	−0.021
Total	0.795	0.851	0.857	0.786	0.841	0.846
CH overlap populations, p						
Total, 3H Avg.	0.747	0.747	0.740	0.737	0.737	0.730
$p\pi$H	0.470	0.459	0.453	0.450	0.439	0.434
$p\sigma$H	0.082	0.081	0.081	0.082	0.081	0.081

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[a] Given in order; zeroth-order, converged with $\omega(\chi_M)$, with $\omega(I-A)$. All C$2p\alpha$ averaged through all cycles. Same notation as used in Tables 3 and 4 of Ref. [1]. [b] Averaged B$2p\alpha$ through all cycles. [c] B$2p\alpha_x$ and $2p\alpha_y$ averaged through all cycles. [d] Largest change in any α on iteration prior to convergence and, in parentheses, number of iterations required.

Examination of the charge distributions which are more directly related to the technique under investigation reveals more easily rationalized effects. In both ω-calculations the population in the formally empty boron orbital ($p_z \equiv \pi$) is increased upon cycling, as is that in each of the boron orbitals involved in the σ-framework, albeit somewhat more weakly. The total charge deficiency for boron is consequently predicted to be only 1/3—1/5 that obtained in the zeroth order (ZO) results. Greater effects are noted for the $I-A$ adjustment scheme, principally due to the larger $2p-\omega$'s which favor charge flow from the electron rich carbons and hydrogens, compared to ethane taken as a norm, to the strongly deficient boron atom. Interestingly the carbon π-orbital, effectively electroneutral in the ZO approximation, nevertheless is predicted to transfer electronic charge upon cycling. This doubtlessly occurs mainly under the influence of the total population density excess of the atom as expressed in the second bracketed term of Eq. (7). The hydrogens are predicted to account $\sim 10\%$ of the total donation to boron in the $\omega(\chi_M)$ adjustment and $\sim 30\%$ when $\omega(I-A)$ is used.

It is not surprising to note that the B–C overlap populations (bond orders) are increased upon cycling. The π-quasi-π component of the total increases because of enhanced donation by carbon to the boron π-orbital. That all other components likewise are increased may be explained in terms of levelling of the differences between the boron and carbon α's. The $B2p\alpha$ values are found, for example, in the $\omega(\chi_M)$ adjustment to have increased in magnitude by ~ 0.05 and the $B2s\alpha$ by ~ 0.10 with smaller decreases noted for the carbon α's. This is accompanied by 4–18% increases in the magnitudes of all the overlap population components and an average of $\sim 7\%$ in the total. On the other hand, the average CH bond order is not much changed by these adjustments. With $\omega(\chi_M)$ no change occurs, and with $\omega(I-A)$ a slight decrease is noted, despite the fact that the OP for the hydrogen most favorably disposed for hyperconjugation is seen to decrease under both adjustment schemes. Examination of the full set of orbital overlap population results, which space limitations preclude showing, indicates that a concurrent increase in the $2s$C–$1s$H OP essentially balances the decrease in the $2p\pi$–$1s$H component in the former adjustment method and nearly does so in the latter. For example, the $2s$C–$1s$H values which pertain for columns 5 and 6 of Table 2 are 0.180 and 0.188, respectively.

Table 3 contains the results obtained for $N(CH_3)_3$ under similar analysis. The only results shown are for the isotropic $N2p\alpha$ starting set obtained by averaging the SCF values from NH_3. Use of the anisotropic set where the NH_3 values are employed directly and the anisotropy is maintained upon redistribution yields very nearly the same results as those shown through all cycles. As for the results themselves, it is not surprising to find that in contrast to $B(CH_3)_3$ adjustment by the $\omega(\chi_M)$ redistribution scheme leads to more profound corrections to the ZO results than by the $\omega(I-A)$ scheme. This is mainly due to the substantially larger ω's for nitrogen in the former than in the latter scheme: the ω-values for the $N2p$ orbitals given in the $(I-A)$ column, it should be recalled, are taken directly from the coefficient value of Eq. (6). The charge redistribution adjustments here improve the agreement between the Koopman's Theorem and observed ionization potentials, in either case to within 0.3 eV of the photoionization value.

Again in contrast to the alkylboron, less severe although still striking changes are noted in the amine populations upon redistribution. The nitrogen atom, predicted to be slightly electron deficient from the ZO results becomes mildly electron rich upon cycling, principally because of increased density in the N2*s* orbital. All of the effect may be attributed to the hydrogens which also increase the density on the carbons substantially. Interestingly, both these species approach, and, in the $I-A$ scheme, surpass, in the self-consistent limits, the electronic distributions they are predicted to have in ethane (i.e., for ethane, $q_H^0 = +0.11$, $q_H^\infty(I-A) = +0.08$). The overlap populations show only small changes upon redistribution. The total C–N populations decrease slightly, paralleling the decrease noted for the π-π population which is predicted to be weakly bonding in the ZO approximation but becomes essentially non-bonding upon redistribution. The effect on the CH populations is at least an order of magnitude smaller and resembles the effects noted in $(CH_3)_3B$ under similar adjustments. The somewhat smaller CH OP's in the amine than in the alkylboron (isotropic model), or in

Table 3. *Zeroth-order and self-consistent MO results for* $(CH_3)_3N$[a]

	ZO	$\omega(\chi_M)$	$\omega(I-A)$
Energies (a.u.)			
$-1/2\,\Sigma\,\varepsilon_i$	57.8060	58.1348	58.0818
HFMO	−0.244	−0.294	−0.280
Convergence[b]	–	$8\times10^{-4}(5)$	$9\times10^{-4}(6)$
Nitrogen, net atomic and orbital charges, q			
$p_z(\pi)$[c]	0.280 (0.378)	0.273 (0.369)	0.279 (0.376)
2*s*	−0.357	−0.481	−0.449
p_x, p_y	0.048	0.030	0.047
Total	0.024	−0.145	−0.071
Methyl group charges, q			
$Cp_z(\pi)$[c]	−0.020	−0.054	−0.064
	(−0.035)	(−0.071)	(−0.075)
C2*s*	−0.188	−0.229	−0.251
C Total	−0.113	−0.218	−0.282
Avg. H	0.035	0.089	0.102
Overlap populations, methyl carbon-nitrogen, p			
$p_z(\pi)-p_z(\pi)$[c]	−0.005	−0.012	−0.011
	(0.010)	(0.002)	(0.003)
Total	0.773	0.734	0.740
CH overlap populations, p			
Total, 3H Avg.	0.7357	0.7351	0.7318
$p_z(\pi)-H$[c]	0.573 (0.500)	0.572 (0.502)	0.571 (0.501)
$p\sigma H$[d]	0.072	0.070	0.071

[a] For the isotropic N2$p\alpha$ case, initial values averaged from NH_3 and averaging continued through all cycles. [b] Largest change in any α on iteration prior to convergence, and in parentheses number of iterations required. [c] Values relating to the Z-(symmetry) axis and, in parentheses, to the direction along the C–N bond. [d] The σ-component, along the CN bond direction, of the C2$p\sigma$–1*s*H overlap population.

ethane itself, was rationalized previously on the basis of decreased 2*s*C–1*s*H terms in the former resulting from influence of the nitrogen [1]; the figures for the *p*–H contributions in Tables 2 and 3 bear out this analysis.

The corresponding figures for the adduct are to be found in Table 4. All important details are judged to be obtainable from the model employing isotropic 2*pα*'s for both boron and nitrogen with $\omega(\chi_M)$ redistribution, and as well under the slightly less stringent convergence limits employed (here set at $<10^{-2}$ compared to 2×10^{-3} for the reactants). As indicated in the table, α-convergence to $<7\times10^{-3}$ was obtained in 3 cycles; central processor time on the CDC 6600 for the total computation on the complex was ~12 minutes.

Rather interesting and empirically satisfying results are obtained from this examination, especially when comparisons are drawn with the charge density effects predicted in the reactants. The extraordinary electron deficiency predicted for the complexed nitrogen from the ZO results is decreased sharply, principally by the establishment of a large excess of electrons in the N2*s* orbital to offset the very strong contribution from its 2*p* orbital to boron. This result does not in any way conflict with the notion of lone-pair donation from nitrogen, which is, as we have previously seen, mainly 2*p* in nature, but removes the need for picturing

Table 4. *Zeroth-order and self-consistent MO results for* $(CH_3)_3B–N(CH_3)_3$ [a]

	ZO		$\omega(\chi_M)$	
Energies (a.u.)				
$-1/2\,\Sigma\,\varepsilon_i$	107.1729		107.6336	
HFMO	−0.372		−0.409	
Convergence[b]	–		$7\times10^{-3}(3)$	
Central atom, net atomic and orbital charges, *q*				
$p_z(\pi)$	−0.661 (−0.666)	0.934 (0.952)	−0.570 (−0.599)	0.865 (0.881)
2*s*	0.340	−0.230	0.194	−0.519
p_x, p_y	0.306	0.054	0.242	0.033
Total	0.293	0.816	0.112	0.286
Methyl group charges, *q*				
$Cp_z(\pi)^c$	−0.059 (−0.053)	−0.012 (−0.033)	−0.055 (−0.057)	−0.037 (−0.081)
C2*s*	−0.379	−0.202	−0.281	−0.220
C Total	−0.594	−0.155	−0.454	−0.180
Avg. H	0.082	0.044	0.098	0.069
Overlap populations, methyl carbons-central atom, *p*				
$p_z(\pi)-p_z(\pi)^c$	−0.024 (−0.013)	−0.012 (−0.000)	−0.023 (−0.012)	−0.016 (−0.008)
Total	0.684	0.774	0.738	0.720
CH overlap populations, *p*				
Total 3H Avg.	0.756	0.7365	0.764	0.7395
$p_z(\pi)-H^c$	0.594 (0.514)	0.581 (0.506)	0.591 (0.513)	0.576 (0.508)
$p\sigma-H^d$	0.079	0.075	0.078	0.070
B–N OP's	Total 0.679, $p\sigma=0.301$,	$p\pi_{quasi}=-0.002$	Total 0.595, $p\sigma=0.288$,	$p\pi_{quasi}=-0.008$

[a] For the averaged boron and nitrogen 2*pα* approximation, cycling with $\omega(\chi_M)$. α averaging continued through all cycles. The left column of the pairs refers to the boron and its substituent methyls, the right to nitrogen and its methyls. Footnotes b–d of Table 3 apply.

the complex in almost formal ionic terms. Viz., in the ZO approximation, nitrogen is $+0.8$ compared to the amine and boron ~ -0.4 compared to $(CH_3)_3B$; under charge redistribution these relative values become $\sim +0.4$ and -0.2, a factor of two smaller. The amount of charge predicted to be transferred in total between the fragments is 0.75 from the ZO results and <0.4 from the $\omega(\chi_M)$ calculations.

Somewhat closer scrutiny of the origin of the donation by nitrogen to the alkylboron fragment upon complexing suggests a push-pull or two-way charge transfer effect is operative. Where in the ZO case one concludes that ~ 0.1 electrons not associated with the p_z orbital are donated in the bond formation, the $\omega(\chi_M)$ results suggest an opposite effect. From the latter results, all orbitals on nitrogen besides p_z are ~ 0.42 electrons rich in the amine, compared to an excess of 0.57 in the adduct (mainly a $2S$ orbital density change, *vide supra*). At the same time, the amine methyls which are ~ 0.15 electrons deficient in total become less so in the adduct by ~ 0.07 electrons. Therefore we may conclude that while ~ 0.58 electrons are being donated from the p_z (main component of the lone-pair) orbital, more than 0.2 electrons are returned by the boron fragment and about 3/4 of this remains on the nitrogen. These insights aid in understanding why the B–N overlap population is found to decrease upon cycling. The $2s$ and $2p\sigma$ α's for both atoms increase in magnitude as charge is redistributed, mainly because of electron donation to the methyls (relative to the standard conditions for these atoms). The values for nitrogen increase more rapidly however because of its lone-pair donation properties. Consequently, what was an imbalance in α's in the ZO computation is heightened and the orbital OP's in general decrease. The one exception $B2sN2p\sigma$ increases in accord with this analysis; the ZO and converged α's (a.u.) are $B2s(-1.081, -1.197)$, $N2p\sigma(-0.334, -0.480)$ and the corresponding orbital OP's are 0.176, 0.182.

The apparent enigma of electron accumulation on the amine carbons with complexing noted in the ZO results is removed in the present calculations. Previously the figures were -0.11 and -0.16 for the total q (per carbon) in $(CH_3)_3N$ and the complex; here they are -0.22 and -0.18.

Based on the foregoing analyses the following modifications are suggested for the VB representations of Ref. [1]. The changes for $(CH_3)_3B$ are mainly concerned with the magnitude of inductive donation by boron to carbon; this should be much weaker, consistent with a drop in total electron deficiency for the boron and the more nearly normal C and H populations, relative to ethane. On the other hand, hardly any vestige of C–N multiple bonding remains in the amine after cycling while more profound inductive donation from the methyls to the nitrogen is called for (i.e., $\delta' > \delta \gg \delta''$). Again, as in the $(CH_3)_3B$ cases, the carbons and hydrogens in the amine appear more conventional, in terms of simple alkane distributions, after charge redistribution. Whether this observation by itself has physical significance is difficult to tell; it is certain however that the large charge imbalances which may be predicted on the basis of faulty or inapplicable parametrization in many MO methods are usually not found in real systems. It seems entirely likely that B_2H_6 and BH_3 are not sufficiently close to $B(CH_3)_3$, and the latter as a component in the adduct, nor NH_3 to $N(CH_3)_3$ in both its forms, to have as much faith in the details computed for them as in what one may obtain for the basis molecules themselves by the method. The methods of charge redistribution examined recognize such differences and attempt to modify their most likely sources (the individual orbital α's) with apparent success, at least with respect to empirical views concerning the distribution of electrons in formally neutral systems. At the same time, it is to be recalled that the redistribution methods are not explicitly parametrized for any part of this system but depend upon different properties for vastly simpler systems (e.g., ionization potentials and electron affinities in isolated atoms). Hence, the following comparisons are in order.

Several of the MO quantities computed for this reaction system were compared with experimental observables in the preceding paper. It would be of interest to update these comparisons with the results obtained allowing charge redistribution to further examine the reliability of redistribution methods employed.

The change in alkyl boron average CH overlap population upon complex formation is predicted to be roughly twice as large from the $\omega(\chi_M)$ scheme as from the ZO results, i.e., from 0.747 to 0.764 compared to 0.747 to 0.756 previously. Since the r_{CH} *vs.* $\mathrm{OP}_{\mathrm{CH}}$ and change in force constant with change in bond length relationships used are roughly linear for small Δr_{CH}, viz.,

$$k = A(r - B)^{-3} \rightarrow \frac{\Delta k}{k} \cong -4\frac{\Delta r}{r}, \tag{8}$$

when $B \cong r_0/4$, an isotope effect roughly twice as great as previously predicted is forthcoming. The effect of $\sim 6\%$ per D is twice that experimentally found. At the same time, the prediction of essentially no deuterium isotope effect in the amine methyls obtained previously is not affected, although in contrast to the ZO results some slight change in the average CH population is now found. The increase in OP predicted (Tables 3 and 4) should correspond to an effect of $\sim 1\%$ (i.e., $K_{\mathrm{D}}/K_{\mathrm{H}} \approx 1.01$ per D). Turning to the comparison drawn with the quadrupole coupling constant of B^{11} in $(\mathrm{CH}_3)_3\mathrm{B}$, an even larger value of q in the p_z orbital on boron is predicted upon redistribution. Where values in the range of $1/8 - 1/4$ electron in this orbital were considered to be consistent with the measured variations accompanying alkyl group variation, the value of 1/3 in the ZO approximation is here found to increase to $\sim 1/2$.

On these bases and recalling of the effect upon the Koopman's Theorem ionization potentials for the reactants, we must conclude that charge redistribution formulated and parametrized in the way proposed, while appearing empirically satisfactory with respect to the charges themselves in the reaction system, does not uniformally improve the correspondence between the theoretical and observable properties of the system. In particular, comparison with the boron-dependent observables are adversely affected. While this is, to be sure, a discouraging result, certain qualifications which place these comparisons in better perspective should be recognized. The comparisons drawn with the observables are very limited and, at least in the case of the isotope effect, are neither completely direct (in the sense of requiring subsidiary and approximate theory) nor capable of improvement (the ZO value $K_{\mathrm{D}}/K_{\mathrm{H}}$ reproduced the experimental values perfectly). At the same time, whereas the method of redistribution formulated on the basis of atomic behavior could be limitedly confirmed and parametrized for carbon- and hydrogen-containing simple molecules, confirmation and parametrization for the other atoms, particularly boron, is not possible from any knowledge for even remotely similar molecular species (viz., the roughly tetrahedral boron atom in the complex).

It would therefore seem fair to reserve judgement on the general efficacy of the charge redistribution methods until further SCF results for appropriate basis molecules become available. These may allow improved parametrization of the forms already adopted (Eqs. 6 and 7), or perhaps suggest more appropriate reformulations either on a rigorous theoretical basis or, less satisfactorily, in a more or less empirical manner as was the case for the ω-technique in the improvement of simple Hückel theory [7]. Application of closed form analysis [12] to some simpler molecular systems is being initiated to test the adequacy of the linear redistribution formulation.

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