# Approximate Self Consistent Field Molecular Orbital Calculations on the Complexes of Trimethylboron, Boron Trichloride, Trimethylaluminium, Alane and Aluminium Trichloride with Trimethylamine

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CNDO/2 calculations have been carried out on the complexes $Me_3BNMe_3$, $Cl_3BNMe_3$, $Me_3AlNMe_3$, $H_3AlNMe_3$ and $Cl_3AlNMe_3$. It is found that the amount of charge transferred from donor to acceptor increases as the substituents on the acceptor become more electronegative. The resulting net negative charge on the acceptor is carried by the substituents, the resulting net positive charge on the donor is carried by the methyl groups.

$\mathbf{I}$t is well known that the chlorides of boron and aluminium are stronger Lewis acids than trimethylboron and trimethylaluminium: Thus the enthalpy of formation of the gaseous complex from the gaseous components

$$BX_3(g) + pyridine(g) = X_3B.pyridine(g)$$
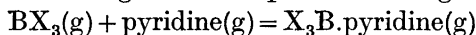
is $\Delta H_f(g) = -17$ kcal/mol for $X = Me$ [1] and $\Delta H_f(g) = -36$ kcal/mol for $X = Cl$.[2] The $B-N$ bond distance in $Cl_3BNMe_3$ is 1.575(11) Å,[3] while the $B-N$ bond distance in $Me_3BNMe_3$ has been estimated to lie in the region 1.70 to 1.90 Å.[4]

Similarly the enthalpy of formation of the gaseous complexes $Me_3AlNMe_3$ and $Cl_3AlNMe_3$ from the gaseous monomeric components are $-30.7 \pm 0.3$ kcal/mol [5,6] and $-47.5 \pm 2.0$ kcal/mol,[6,7] respectively. The $Al-N$ bond distance in $Cl_3AlNMe_3$ is 1.96(1) Å [8] while the $Al-N$ bond distance in $Me_3AlNMe_3$ is 2.099(10) Å.[6]

This variation of Lewis acid strength has been interpreted as an inductive effect.[9] In order to obtain clues into the manner in which it operates we have performed a series of approximate self consistent field molecular orbital calculations on the complexes of $BMe_3$, $BCl_3$, $AlMe_3$, and $AlCl_3$ with $NMe_3$ and on some related species.

The enthalpy of formation of $H_3AlNMe_3$ is not known, but the magnitude of the $Al-N$ bond distance, 2.063(11) Å,[10] indicates that the Lewis acid strength of $AlH_3$ is intermediate between that of $AlMe_3$ and $AlCl_3$. This is indeed to be expected if an inductive effect was dominant, and calculations were therefore performed on this complex and related species as well.

## CALCULATIONS

The main structure parameters of the species considered are listed in Table 1. The $C-H$ bond distance and the $\angle N-C-H$ valence angle in free $NMe_3$ [11] was assumed to remain unaltered in the complexes and in $NMe_4^+$.

*Table 1.* Structure parameters of the species $NMe_3$, $NMe_4^+$, $MX_3$, $MX_4^-$ and the complexes $X_3MNMe_3$.

|  | $R(X-M)$ (Å) | $\angle X-M-C_3$ (°) | $R(M-N)$ (Å) | $\angle C_3-N-C$ (°) | $R(N-C)$ (Å) | Ref. |
|---|---|---|---|---|---|---|
| $NMe_3$ |  |  |  | 108.3 | 1.454 | 11 |
| $NMe_4^+$ |  |  |  | α | 1.499 | 12 |
| $BMe_3$ | 1.578 | 90 |  |  |  | 13 |
| $BMe_4^-$ | 1.65 | α |  |  |  | ass |
| $Me_3BNMe_3$ | 1.60 | 109.6 | 1.70 | 110.8 | 1.502 | ass |
| $BCl_3$ | 1.742 | 90 |  |  |  | 14 |
| $BCl_4^-$ | 1.81 | α |  |  |  | ass |
| $Cl_3BNMe_3$ | 1.831 | 109.6 | 1.575 | 110.8 | 1.502 | 3 |
| $AlMe_3$ | 1.957 | 90 |  |  |  | 15 |
| $AlMe_4^-$ | 2.023 | α |  |  |  | 16 |
| $Me_3AlNMe_3$ | 1.987 | 102.3 | 1.099 | 109.3 | 1.474 | 6 |
| $AlH_3$ | 1.54 | 90 |  |  |  | ass |
| $AlH_4^-$ | 1.58 | α |  |  |  | ass |
| $H_3AlNMe_3$ | 1.560 | 104.3 | 2.063 | 109.0 | 1.476 | 10 |
| $AlCl_3$ | 2.06 | 90 |  |  |  | 17 |
| $AlCl_4^-$ | 2.13 | α |  |  |  | 18 |
| $Cl_3AlNMe_3$ | 2.123 | 107.0 | 1.96 | 110.3 | 1.50(ass) | 8 |

α = tetrahedral angle; ass = assumed.

Similarly the $C-H$ bond distances and the $\angle B-C-H$ and $\angle Al-C-H$ valence angles of free $BMe_3$ [13] and $AlMe_3$ [15] were assumed to remain unaltered in the complexes and in $BMe_4^+$ and $AlMe_4^+$.

The MO calculations were carried out in the CNDO/2 approximation with standard values for all parameters.[19,20] The calculations on species containing Al or Cl were carried out with two bases, one (*sp*) consisting only of valence shell Slater type *s* and *p* atomic orbitals, the other (*spd*) including Slater type $3d$ orbitals on Al and Cl with the same orbital exponent ($Z' = 3.50$ for Al, $Z' = 6.10$ for Cl) as the $3s$ and $3p$ orbitals.

## RESULTS AND DISCUSSION

*Charge distribution and dipole moment.* The atomic charges (in 0.01 electron units) obtained for $Me_3BNMe_3$ and $Cl_3BNMe_3$ and related species, the charge transferred from donor to acceptor ($q_{transf}$) and the dipole moments are displayed in Fig. 1. For the species containing Cl the first number has been obtained with the (*sp*), the second with the (*spd*) basis. The calculated dipole
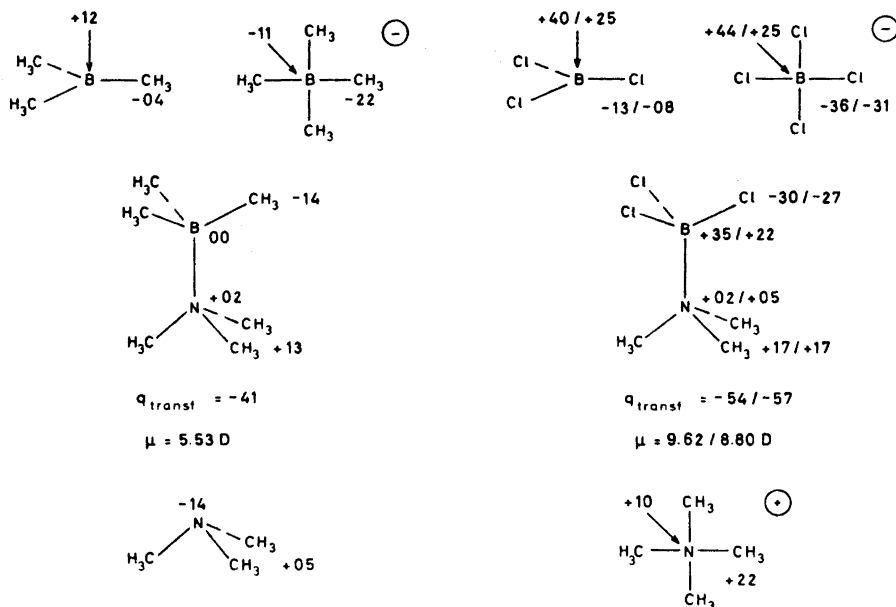
*Fig. 1.* Atomic charges (in 0.01 electron units) obtained for $Me_3BNMe_3$ and $Cl_3BNMe_3$ and related species, the charge transferred from donor to acceptor ($q_{transf}$) and the dipole moments. For the species containing Cl the first number has been obtained with the (*sp*), the second with the (*spd*) basis.

moments of the complexes are in reasonable agreement with the values obtained by measurement on benzene solutions, $3.92 \pm 0.03$ D for $Me_3BNMe_3$ [21] and $6.28 \pm 0.02$ D for $Cl_3BNMe_3$.[22]

The empirical parameters used in CNDO calculations have been carefully calibrated for first row elements and hydrogen,[20] while the parameters for second row elements have been obtained by rough approximations.[19] The most reliable results are therefore obtained by calculations on species consisting of first row elements and hydrogen only.

In particular there is uncertainty as to the proper size of the $3d$ orbitals of second row elements, *i.e.* as to the proper magnitude of the orbital exponent. In calculations with the (*sp*) basis the influence of the $3d$ orbitals is neglected altogether. In the (*spd*) basis the $3d$ orbitals have certainly become too compact, and their importance will be overestimated. One may hope therefore that the values computed for various molecular properties by calculations with both bases will bracket the real value.

It is seen that the positive charge on the B atom in $BCl_3$, $BCl_4^-$, and $Cl_3BNMe_3$ decreases with 0.1 to 0.2 electron units when $d$-orbitals are included in the basis. Inspection of the electron density matrix of $BCl_3$ shows that this is the result of changes both in the $\sigma$ and $\pi$ components of the $B-Cl$ bond.

All the charges calculated, and particularly those of the species containing Cl, must be regarded as uncertain. Nevertheless the fact that they are in perfect agreement with the speculations below must be regarded as giving them some weight.

The B atom in BMe$_3$ carries a small positive charge. Formation of the complex leads to the transfer of 0.4 units of negative charge from the donor. About one fourth of this charge remains located on the B atom, the rest is passed on to the three methyl groups. In the complex, therefore, the boron atom is essentially neutral while the net positive charge on the acceptor is carried by the substituents.
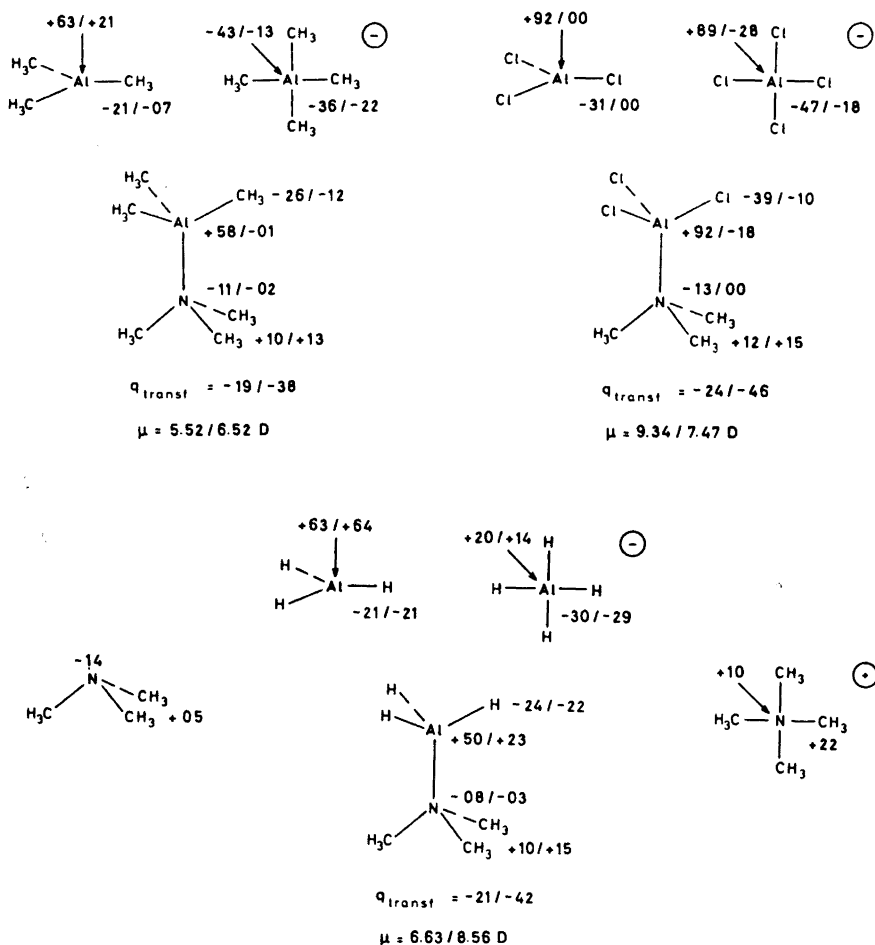


Fig. 2. Atomic charges (in 0.01 electron units) obtained for Me$_3$AlNMe$_3$, H$_3$AlNMe$_3$, and Cl$_3$AlNMe$_3$ and related species, the charge transferred from donor to acceptor ($q_{transf}$) and the dipole moments. The first number in each case has been obtained with the (sp), the second with the (spd) basis.

Substitution of the Me groups in $BMe_3$ by the more electronegative Cl atoms increases the positive charge on B to about 0.3 in $BCl_3$. The more electronegative Cl atom not only allows more negative charge to be transferred from the donor during complex formation, but also allows the B atom to pass nine tenths of the charge received on to the substituents with the result that it retains its positive charge and that the Cl atoms carry the corresponding negative charge in addition to the net negative charge on the acceptor.

While the N atom in free $NMe_3$ carries a small negative charge, the transfer of charge during complex formation leaves the N atom essentially neutral in the complexes while the net positive charge on the donor is carried by the Me groups.

The atomic charges of the complexes $Me_3AlNMe_3$, $H_3AlNMe_3$, and $Cl_3AlNMe_3$ are displayed in Fig. 2. The calculated dipole moments of $H_3AlNMe_3$ are in tolerable agreement with the experimental dipole moment in cyclohexane solution, $4.11 \pm 0.08$ D.[23] Again the first number in each case has been obtained by calculations with the $(sp)$ basis. It is seen that the inclusion of the $3d$ orbitals has a great impact on the charge distribution: The charge on the Al atom in $AlCl_3$, $AlCl_4^-$, and $Cl_3AlNMe_3$ becomes more negative by about one electron unit, the charge on the Al atom in $AlMe_3$, $AlMe_4^-$, and $Me_3AlNMe_3$ becomes more negative by half an electron unit, while the charge on Al in $H_3AlNMe_3$ becomes more negative by a quarter of an electron unit. Only in $AlH_3$ and $AlH_4^-$ do the charges remain nearly unaltered.

This is not to say that the Al $3d$ orbitals do not appear with appreciable coefficients in the MO's of $AlH_3$ and $AlH_4^-$, they do, but only that the coefficient of the hydrogen $1s$ orbital remains unchanged.

Inspection of the density matrices of $AlMe_3$ and $AlCl_3$ again shows that the variation of the calculated charges is the result of change in both the $\sigma$ and $\pi$ components of the $Al - Me$ and $Al - Cl$ bonds.

Clearly the calculated charges for the alane complexes are too uncertain to warrant a detailed discussion. It should nevertheless be noted that they are in agreement with the following general hypotheses:

(i) The amount of charge transferred from donor to acceptor increases as the substituents on the acceptor become more electronegative.

(ii) The acceptor atom remains positively charged or neutral in the complex. The net negative charge is carried by the substituents.

(iii) The N atom in the donor is neutral or carries a small negative charge in the complex. The net positive charge on the donor is carried by the methyl groups.

In all the five complexes that have been studied it has been found that the net negative charge on the acceptor is distributed in such a way that the atomic charges are intermediate between those of the free acceptor and the corresponding "ate" ion, while the atomic charges on the donor are intermediate between those of free $NMe_3$ and $NMe_4^+$.

*Binding energies.* The calculated binding energies of the complexes, defined as the energy of the complex minus the sum of the energies of the free monomeric acceptor and the free donor, are listed in Table 2 along with the observed enthalpies of formation.

*Table 2.* Calculated binding energies (BE) and observed enthalpies of formation of the gaseous complexes from gaseous monomeric acceptor and donor (in kcal/mol).

|                     | BE($sp$) | BE($spd$) | $\Delta H_f$(obs) | Ref. |
|---------------------|----------|-----------|-------------------|------|
| Me$_3$BNMe$_3$      | $-95$    |           | $-18$             | 24   |
| Cl$_3$BNMe$_3$      | $-183$   | $-192$    |                   |      |
| Me$_3$AlNMe$_3$     | $+18$    | $-125$    | $-31$             | 5, 6 |
| H$_3$AlNMe$_3$      | $+12$    | $-159$    |                   |      |
| Cl$_3$AlNMe$_3$     | $+84$    | $-119$    | $-48$             | 6, 7 |

It is seen that calculations with the ($sp$) basis fail to predict the stability of the three alane complexes. This does not mean that the $3d$ orbitals necessarily must be included in the basis if stable complexes are to be predicted; very likely this could be achieved through change of one or more empirical parameters. The binding energies of the alane complexes calculated with the ($spd$) basis and those calculated for the borane complexes with either basis grossly overestimate the strength of the complexes.

*Equilibrium $M-N$ bond distances.* The equilibrium $B-N$ and $Al-N$ bond distances were determined by performing a series of calculations with varying $M-N$ bond distance, but with donor and acceptor geometries unchanged. The results are listed in Table 3.

*Table 3.* Calculated and observed $M-N$ bond distances (in Å).

|                     | $R_{\mathrm{calc}}(sp)$ | $R_{\mathrm{calc}}(spd)$ | $R$(obs)      | Ref. |
|---------------------|-------------------------|--------------------------|---------------|------|
| Me$_3$BNME$_3$      | 1.61                    | —                        | $1.70-1.90$   | 4    |
| Cl$_3$BNMe$_3$      | 1.55                    | 1.52                     | 1.58          | 3    |
| Me$_3$AlNMe$_3$     | Unstable                | 2.12                     | 2.10          | 6    |
| H$_3$AlNMe$_3$      | »                       | 2.06                     | 2.06          | 10   |
| Cl$_3$AlNMe$_3$     | »                       | 2.07                     | 1.96          | 8    |

In agreement with the results discussed in the preceding section it was found that the energies of the three alane complexes calculated with the ($sp$) basis decreased monotonically as the $Al-N$ distances were increased from 1.60 Å to 2.50 Å. With the ($spd$) basis the $Al-N$ bond distances calculated for the Me$_3$AlNMe$_3$ and H$_3$AlNMe$_3$ complexes are very close to the experimental values, while the bond distance calculated for Cl$_3$AlNMe$_3$ is 0.11 Å too long.

The calculations do predict that the $B-N$ bond distance in Me$_3$BNMe$_3$ is longer than in Cl$_3$BNMe$_3$, but in both cases the calculated bond distance is too short.

*Barriers to internal rotation.* The barriers to internal rotation about the $M-N$ bonds were calculated as the energy of the eclipsed molecule minus the energy of the staggered molecule. Hence a positive barrier implies a staggered, a negative barrier an eclipsed equilibrium conformation. Barriers were calculated with the $M-N$ distance fixed at the experimental values with both bases and with the $M-N$ equilibrium distance calculated for the staggered molecule and the ($spd$) basis. The results are shown in Table 4.

*Table 4.* Calculated and observed barriers to internal rotation about $M-N$ bonds (in kcal/mol).

| | $V_0(sp)$ $R = R(\text{obs})$ | $V_0(spd)$ | | $V_0(\text{obs})$ | Ref. |
|---|---|---|---|---|---|
| | | $R = R_{\text{obs}}$ | $R = R_{\text{calc}}(spd)$ | | |
| $Me_3BNMe_3$ | $+1.7$ | $-$ | $+2.4$ | | |
| $Cl_3BNMe_3$ | $+6.8$ | $-3.3$ | $-3.8$ | | |
| $Me_3AlNMe_3$ | $+2.0$ | $5.3$ | $5.0$ | $>0$ | 6 |
| $H_3AlNM_3$ | $+1.4$ | $3.7$ | $3.7$ | $>0$ | 10 |
| $Cl_3AlNMe_3$ | $+2.9$ | $4.2$ | $3.4$ | $>0$ | 25 |

In every instance it was found that the electronic energy is lowest in the eclipsed conformation while the core repulsion energy is lowest in the staggered conformation. In every instance except $Cl_3BNMe_3$ with an $(spd)$ basis the core repulsion energy dominates, and the calculations predict a staggered equilibrium conformation. More accurate calculations have shown similar conditions to prevail in $H_3BNH_3$.[26]

The three species for which experimental information is available are indeed staggered in the gas phase.

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