Theoret. chim. Acta (Berl.) 11, 344—357 (1968)

Quantum Mechanical Calculations on Barriers to Internal Rotation

II. The Borazane Molecule BH_3-NH_3

M.-CL. MOIREAU
Laboratoire de Chimie E.N.S.J.F., 24 rue Lhomond, Paris 5°, France

A. VEILLARD
IBM Research Laboratory, Monterey and Cottle Rds., San José, California 95114

Received April 29, 1968

SCF LCAO MO calculations are reported for the borazane molecule BH_3NH_3, for different values of the dihedral angle (0°, 20°, 40°, 60°). The lower energy was found equal to —82.59651 a.u. for the staggered form. The theoretical barrier height, 0.00524 a.u. = 3.29 kcal/mole, is very close to the one, 0.00577 a.u., computed by Clementi for the ethane molecule. A study of the electronic density maps seems to indicate that some care should be exercised in the use of the population analysis. According to the criterion of Bader and *al.*, the bond density map seems characteristic of ionic binding.

Die Ergebnisse von SCF LCAO MO Rechnungen für Borazan werden mitgeteilt, und zwar für verschiedene Verdrillungswinkel. Die tiefste Energie zeigt die Konformation mit den auf Lücke stehenden H-Atomen. Die Energieschwelle für die innere Rotation ist mit 3.29 Kcal/mol fast genau so groß wie die (von Clementi berechnete) für Äthan.

Das Bindungsdichte-Diagramm deutet bei Anwendung des Baderschen Kriteriums auf eine ionische Bindung hin. Eine Untersuchung der Elektronendichte legt ferner die Vermutung nahe, daß die Resultate einer Populationsanalyse mit Vorsicht betrachtet werden müssen.

La molécule de borazane a été etudiée par la méthode SCF LCAO MO pour différentes valeurs de l'angle dièdre (0°, 20°, 40°, 60°). L'énergie la plus basse, égale à —82.59651 u.a., a été obtenue pour la conformation decalée. La barrière de rotation théorique, égale à 0.00524 u.a. = 3.29 kcal/mole, est très proche de la valeur 0.00577 u.a. obtenue par Clementi pour la molécule d'éthane. L'étude simultanée de l'analyse de population et des contours de densité isoélectronique semble indiquer qu'une certaine prudence s'impose dans l'interprétation des populations. La liaison B—N apparait comme ionique si l'on on utilise les critères de Bader *et al.*

1. Introduction

The nature of the barrier of internal rotation has been recently studied for molecules of the type AH_m–BH_n through the use of *ab-initio* calculations. The first calculation was made by Pitzer and Lipscomb [15] for ethane, using a minimal Slater basis set. Then Clementi reinvestigated the problem [2], using a fairly large Gaussian basis set: both calculations gave results in good agreement with experimental values. It should be pointed out that C_2H_6 corresponds to a very simple situation with respect to the problem of the internal rotation barrier: the molecule shows a high symmetry, the C–C bond can be thought of as a typical covalent bond, and the six hydrogen atoms are strictly equivalent. One can easily be persuaded that the staggered form is highly favored because of the repulsions between the protons at the two ends of the molecule [10]. Then came a series of calculations about less simple cases: hydrazine [19, 5, 14], hydrogen peroxyde [9, 4, 14, 13], methylalcohol [4, 14], and methylamine [4, 14]. As a result, the situation appeared less and less satisfactory: this is evidenced for hydrogen peroxyde, since the numerous calculations have been unable either to give the height of the barrier or to predict the minimum of the energy curve. This poor agreement can probably be traced to the interaction between lone pairs, since it occurs only for hydrogen peroxyde and possibly for hydrazine.

In all the above examples of barriers to internal rotation, either the molecule was symmetrical with equivalent hydrogen atoms at the two ends (for C_2H_6, N_2H_4, H_2O_2) or the hydrogen atoms attached to the A and B atoms were expected to bear formal charges of the same sign (CH_3OH, CH_3NH_2).

A much simpler situation should occur in the borazane molecule BH_3NH_3. Like H_2O_2 or N_2H_4, BH_3–NH_3 is isoelectronic to ethane. However, a clearer picture should emerge from the lack of lone pair and comparison with ethane will be made much easier by the equal number of hydrogen atoms. With respect to the ethane molecule, the only factor which can affect the rotational barrier is the different nature of the central bond, which brings some difference between the hydrogen atoms on the two ends of the molecule. A previous calculation for the borazane molecule [20] showed that the hydrogen atoms attached to the boron atom have a negative population (-0.1 e) while the hydrogen atoms bound to nitrogen are positively charged ($+0.37$ e). One could wonder if some electrostatic attraction between the opposite formal charges at the two ends of the molecule would not lower the barrier with respect to the value in ethane. One can also wonder what is the effect on the rotational barrier of an A–B bond which is probably not covalent in nature.

None of the previously quoted calculations of barriers to internal rotation have reached the Hartree-Fock limits. Few included $2p$ polarization functions on the hydrogen atoms (attempts were made for H_2O_2 [4, 14] and for C_2H_6 [14]) while none included $3d$ polarization functions on the carbon, nitrogen or oxygen atoms. From the experience gained with ethane [15, 2] or with hydrogen peroxyde [9, 4, 13, 14], it seems that the computed barrier is relatively insensitive to the choice of the basis set for the s and p orbitals, provided that the size of the basis set is large enough to insure reasonable results. However, the effect of the inclusion of $3d$ polarization functions on the barrier has never been investigated. The previous calculation for borazane (which was restricted to the staggered form) used a restricted basis set built only of s and p-type orbitals [20]. The present calculation not only increases the number of s and p orbitals for the H, B and N atoms, but also includes $3d$ polarization functions for the B and N atoms.

One aim of this calculation was to compute the barrier to internal rotation of borazane, which is experimentally unknown, and to discuss the possible relationship with the barrier in ethane. Another purpose was to get some insight into the electronic nature of the B–N bond of borazane. This molecule is frequently quoted as a typical example of a dative bond: this means that, during molecular formation, a lone pair belonging to a donor group becomes shared with an acceptor group. This sharing results in the bond formation and is expected to bring about a marked rearrangement of the electronic structure. In order to discuss these electronic arrangements, the BH_3 and NH_3 molecules have been studied with the same basis sets and geometry.

It should be emphasized that a satisfactory treatment of the barriers to internal rotation is a first step towards a more general field. This would include also inversion barriers with respect to nitrogen [8, 21] or phosphorus, ring inversion barriers, etc.

2. Description of Computations

Using the general program IBMOL [3], computations were performed for four conformations of the borazane molecule. Four different values, 0° (eclipsed form), 20°, 40°, 60° (staggered form), were used for the dihedral angle (defined as the angle of two planes going through the B–N axis and bisectors of one H–N–H angle and of one H–B–H angle). The corresponding bond lengths were taken from Ref. [7]:

Table 1. *Uncontracted gaussian set for* BH_3NH_3

Center	Type	Indices	Orbital exponent
B	*s*	1	2788.41
B	*s*	2	419.039
B	*s*	3	96.4683
B	*s*	4	28.0694
B	*s*	5	9.37597
B	*s*	6	3.40623
B	*s*	7	1.30566
B	*s*	8	0.32448
B	*s*	9	0.10219
N	*s*	10	5905.44
N	*s*	11	887.451
N	*s*	12	204.749
N	*s*	13	59.8376
N	*s*	14	19.9981
N	*s*	15	7.19274
N	*s*	16	2.68598
N	*s*	17	0.70004
N	*s*	18	0.21329
H(1), H(2), H(3), H(4), H(5), H(6)	*s*	19, 23, 27, 31, 35, 39	13.3615
H(1), H(2), H(3), H(4), H(5), H(6)	*s*	20, 24, 28, 32, 36, 40	2.0133
H(1), H(2), H(3), H(4), H(5), H(6)	*s*	21, 25, 29, 33, 37, 41	0.453757
H(1), H(2), H(3), H(4), H(5), H(6)	*s*	22, 26, 30, 34, 38, 42	0.123317
B	*x, y, z*	43, 53, 63	11.3413
B	*x, y, z*	44, 54, 64	2.43599
B	*x, y, z*	45, 55, 65	0.68358
B	*x, y, z*	46, 56, 66	0.21336
B	*x, y, z*	47, 57, 67	0.070114
N	*x, y, z*	48, 58, 68	26.786
N	*x, y, z*	49, 59, 69	5.95635
N	*x, y, z*	50, 60, 70	1.7074
N	*x, y, z*	51, 61, 71	0.53136
N	*x, y, z*	52, 62, 72	0.16537
B	*xx, xy, xz, yy, yz, zz*	73, 75, 77, 79, 81, 83	1.5
N	*xx, xy, xz, yy, yz, zz*	74, 76, 78, 80, 82, 84	1.5

B–N = 1.56 Å (experimental bond length in borazane),
B–H = 1.19 Å (average B–H bond length),
N–H = 1.012 Å (experimental bond length in ammonia).

The angles were assumed to be tetrahedral. Bond lengths and bond angles were kept the same for the two configurations.

Limitation in the size of the basis set used were imposed by the length of the computations. This consideration prevented us from using *p*-type orbitals for the hydrogen atoms and the Gaussian basis set was chosen as

9 *s*, 5 *p*, 1 *d* atomic functions for both the boron and nitrogen atoms
4 *s* atomic functions for the hydrogen atoms.

In Table 1, we report the atomic Gaussian set used for both the eclipsed and staggered configurations, the orbital exponents and their symmetry type (*s*, *p*, *d*). The 84 gaussians used in our calculation (except the *d* orbitals) have orbital exponents optimized for the ^2S hydrogen, ^4S nitrogen and ^2P boron atoms [6]. These 84 gaussians are then reduced to 44 contracted gaussians [3] which are reported in Table 2. This contraction uses the expansion coefficients obtained

Table 2. *Contracted gaussian set for* BH_3NH_3[a]

Contracted gaussian	Type	Center
$\gamma_1 = 0.00129\beta_1 + 0.00983\beta_2 + 0.04763\beta_3 + 0.16002\beta_4 + 0.36273\beta_5$	s; $1s$	B
$\gamma_2 = 0.43331\beta_6 + 0.14005\beta_7$	s; $1s'$	B
$\gamma_3 = \beta_8$	s; $2s$	B
$\gamma_4 = \beta_9$	s; $2s'$	B
$\gamma_5 = 0.00119\beta_{10} + 0.00909\beta_{11} + 0.04411\beta_{12} + 0.15043\beta_{13} + 0.35658\beta_{14}$	s; $1s$	N
$\gamma_6 = 0.44611\beta_{15} + 0.14553\beta_{16}$	s; $1s'$	N
$\gamma_7 = \beta_{17}$	s; $2s$	N
$\gamma_8 = \beta_{18}$	s; $2s'$	N
$\gamma_9 = 0.01906\beta_{19} + 0.13424\beta_{20} + 0.47449\beta_{21}$	s; $1s$	H(1)
$\gamma_{10} = \beta_{22}$	s; $1s'$	H(1)
$\gamma_{21} = 0.01435\beta_{43} + 0.08803\beta_{44} + 0.30565\beta_{45}$	x; $2p_x$	B
$\gamma_{22} = 0.51687\beta_{46} + 0.30564\beta_{47}$	x; $2p'_x$	B
$\gamma_{23} = 0.01452\beta_{48} + 0.09258\beta_{49} + 0.31026\beta_{50}$	x; $2p_x$	N
$\gamma_{24} = 0.50679\beta_{51} + 0.31773\beta_{52}$	x; $2p'_x$	N
$\gamma_{25} = 0.01435\beta_{53} + 0.08803\beta_{54} + 0.30565\beta_{55}$	y; $2p_y$	B
$\gamma_{26} = 0.51687\beta_{56} + 0.30567\beta_{57}$	y; $2p'_y$	B
$\gamma_{27} = 0.01452\beta_{58} + 0.09258\beta_{59} + 0.31026\beta_{60}$	y; $2p_y$	N
$\gamma_{28} = 0.50679\beta_{61} + 0.31773\beta_{62}$	y; $2p'_y$	N
$\gamma_{29} = 0.01435\beta_{63} + 0.08803\beta_{64} + 0.30565\beta_{65}$	z; $2p_z$	B
$\gamma_{30} = 0.51687\beta_{66} + 0.30567\beta_{67}$	z; $2p'_z$	B
$\gamma_{31} = 0.01452\beta_{68} + 0.09258\beta_{69} + 0.31026\beta_{70}$	z; $2p_z$	N
$\gamma_{32} = 0.50679\beta_{71} + 0.31773\beta_{72}$	z; $2p'_z$	N
$\gamma_{33} = \beta_{73}$ $\gamma_{34} = \beta_{74}$		B, N
$\gamma_{35} = \beta_{75}$ $\gamma_{36} = \beta_{76}$		B, N
$\gamma_{37} = \beta_{77}$ $\gamma_{38} = \beta_{78}$		B, N
$\gamma_{39} = \beta_{79}$ $\gamma_{40} = \beta_{80}$		B, N
$\gamma_{41} = \beta_{81}$ $\gamma_{42} = \beta_{82}$		B, N
$\gamma_{43} = \beta_{83}$ $\gamma_{44} = \beta_{84}$		B, N

[a] Note: γ_{11} to γ_{20} are not reported since there is a one-to-one correspondence between $(\gamma_{11}, \gamma_{12})$, $(\gamma_{13}, \gamma_{14})$, $(\gamma_{15}, \gamma_{16})$, $(\gamma_{17}, \gamma_{18})$, $(\gamma_{19}, \gamma_{20})$ and (γ_9, γ_{10}).

from the computation of the separated atoms [6]. From this contracted set we construct the symmetry adapted functions which transform according to the irreducible representations of the C_{3v} symmetry group. The following configuration was used for the electronic structure of the ground state:

$$(1a_1)^2\,(2a_1)^2\,(3a_1)^2\,(1e)^4\,(4a_1)^2\,(5a_1)^2(2e)^4\,.$$

As said already, similar calculations were performed for the NH_3 and BH_3 (hypothetical unplannar) molecules, using the same geometry, i.e. the same bond length with tetrahedral angles, the same gaussian basis set and the same set of contracted functions.

3. Numerical Results

For the staggered and eclipsed conformations, the total energies and orbital energies are given in Table 3. In a first set of computations (called *A*) the *d*-orbitals were deleted from all the irreducible representations, while in a second set of computations (called *B*) they were introduced for the B and N atoms. This was done in order to ascertain the effect of the 3*d* polarization functions on the rotational barrier. Total energies for sets *A* and *B* and dihedral angles of 0° (eclipsed), 20°, 40°, 60° (staggered) are found in Table 4. In Tables 5 and 6 are summarized the results obtained respectively for the BH_3 and the NH_3 molecules. The gross orbital populations [12] and the gross atomic charges are reported in Tables 7, 8, and 9.

Energy results for the four conformations described above were fitted by a function of the dihedral angle φ

$$E_t(\varphi) = a_0 + a_1 \cos 3\varphi + a_2 \cos 6\varphi + a_3 \cos 9\varphi$$

with the following values of a_0, a_1, a_2, a_3:

$$a_0 = -82.577032 \qquad a_1 = 0.002555 \qquad a_2 = 0.000005 \qquad a_3 = 0\,.$$

for the set *A* of computations (without *d* orbitals),

$$a_0 = -82.593895 \qquad a_1 = 0.002621 \qquad a_2 = 0.000005 \qquad a_3 = 0\,.$$

for the set *B* of computations (with *d* orbitals).

Table 3. *Total energy and orbital energies for* BH_3NH_3 *staggered and eclipsed (in a.u.)*

	Staggered		Eclipsed	
	A	*B*	*A*	*B*
Total energy	−82.57958	−82.59651	−82.57447	−82.59127
$E(1a_1)$	−15.66195	−15.66107	−15.65994	−15.65911
$E(2a_1)$	− 7.51497	− 7.51131	− 7.51466	− 7.51099
$E(3a_1)$	− 1.27260	− 1.27047	− 1.27229	− 1.27019
$E(1e)$	− 0.74669	− 0.74821	− 0.74670	− 0.74824
$E(4a_1)$	− 0.72978	− 0.72953	− 0.72934	− 0.72913
$E(5a_1)$	− 0.53044	− 0.53129	− 0.53051	− 0.53140
$E(2e)$	− 0.40182	− 0.40338	− 0.40056	− 0.40205

Table 4. *Total energy of* BH_3NH_3*(in a.u.) as a function of the dihedral angle*

	(*A*)	(*B*)
$\varphi = 0°$	−82.574472	−82.591268
$\varphi = 20°$	−82.575757	−82.592587
$\varphi = 40°$	−82.578312	−82.595208
$\varphi = 60°$	−82.579583	−82.596511

Table 5. SCF *results for* BH_3

	A	*B*
Total energy	−26.33797	−26.34169
$E(1a_1)$	− 7.62992	− 7.62731
$E(2a_1)$	− 0.71875	− 0.71772
$E(1e)$	− 0.48370	− 0.48422

Table 6. SCF *results for* NH_3

	A	*B*
Total energy	−56.15626	−56.17093
$E(1a_1)$	−15.52007	−15.51732
$E(2a_1)$	− 1.12940	− 1.12326
$E(1e)$	− 0.61788	− 0.61881
$E(3a_1)$	− 0.40474	− 0.40829

Table 7. *Gross population analysis for* BH_3NH_3

	Staggered				Eclipsed			
	B	N	H_B	H_N	B	N	H_B	H_N
Calculation A								
s	2.9295	3.5580	1.0472	0.6364	2.9300	3.5588	1.0568	0.6348
$2p_x, 2p_y$	0.9411	1.3135			0.9264	1.3169		
$2p_z$	0.3478	1.6048			0.3459	1.6041		
Total	5.1594	7.7898	1.0472	0.6364	5.1287	7.7967	1.0568	0.6348
Atomic charge	−0.1594	−0.7898	−0.0472	+0.3636	−0.1287	−0.7967	−0.0568	+0.3652
Calculation B								
s	2.9308	3.5499	1.0456	0.6369	2.9313	3.5507	1.0552	0.6353
$2p_x, 2p_y$	0.9375	1.3107			0.9228	1.3142		
$2p_z$	0.3548	1.5943			0.3528	1.5935		
$3d_{xx,yy}$	0.0034	0.0036			0.0033	0.0036		
$3d_{xy}$	0.0017	0.0033			0.0017	0.0032		
$3d_{xz,yz}$	0.0010	0.0030			0.0010	0.0031		
$3d_{zz}$	0.0004	−0.0011			0.0004	−0.0011		
Total	5.1713	7.7811	1.0456	0.6369	5.1405	7.7880	1.0552	0.6353
Atomic charge	−0.1713	−0.7811	−0.0456	+0.3631	−0.1405	−0.7880	−0.0552	+0.3647

Table 8. *Gross population analysis for* BH_3

		s	$2p_x, 2p_y$	$2p_z$	$3d_{xx}, 3d_{yy}$	$3d_{xy}$	$3d_{xz}, 3d_{yz}$	$3d_{zz}$	Total
(*A*)	B	3.1291	0.9902	0.0295					5.1389
	H	0.9537							0.9537
(*B*)	B	3.1292	0.9860	0.0290	0.0060	0.0018	0.0006	−0.0046	5.1406
	H	0.9531							0.9531

Table 9. *Gross population analysis for* NH_3

		s	$2p_x, 2p_y$	$2p_z$	$3d_{xx}, 3d_{yy}$	$3d_{xy}$	$3d_{xz}, 3d_{yz}$	$3d_{zz}$	Total
(*A*)	N	3.6105	1.1804	1.8348					7.8062
	H	0.7313							0.7313
(*B*)	N	3.5987	1.1861	1.8222	0.0108	0.0032	0.0033	−0.0089	7.8156
	H	0.7281							0.7281

4. Discussion

As for ethane, the staggered form is the most stable conformation. The corresponding energy, −82.59651 a.u., is appreciably lower than the one reported previously, −82.529 a.u. [20]. This is related to the use of a larger basis set, and a noticeable amount of the improvement, 0.017 a.u. out of 0.067 a.u., is due to the introduction of the 3*d* orbitals. It is not possible to tell exactly how far this calculation is from the Hartree-Fock limit. However, we can get some idea from the result for the NH_3 molecule. This calculation gave for NH_3 a total energy of −56.17093 a.u., while the Hartree-Fock limit has been estimated as −56.23 a.u. by Ritchie and King [16].

The height of the barrier to internal rotation is found equal to 0.00524 a.u. = 3.290 kcal/mole. This is very similar to the value obtained by Clementi [2] for the ethane molecule: 0.00577 a.u. It should be noticed that the barrier does not seem very sensitive to a particular choice of the basis set: the *A* computation (without *d* orbitals) gives a barrier height of 0.00511 a.u. = 3.207 kcal/mole, so that the relative variation is only three percent. This had already been pointed out by Clementi [2]: including polarization functions (limited here to the 3*d* orbitals) gives a real improvement for total energies, but the effect is of much less importance for the determination of the barrier height.

From the expression of the potential energy as a function of the dihedral angle, it is clear that the barrier is very close to the cosine function in shape. Similar values have been found previously by Clementi and Davis for the a_1, a_2 and a_3 coefficients in the ethane molecule [2]:

$$a_0 = -79.10534 \qquad a_1 = +0.00289 \qquad a_2 = -0.00001 \qquad a_3 = 0\,.$$

According to Wyatt and Parr [22], the electronic component of the internal rotation barrier in ethane can be interpreted as though it comes from regions around protons. C–H orbitals alone would contribute almost the entire electronic part of the rotational barrier in ethane and the C–C bond orbital would play an insignificant role in producing the rotational barrier. This view seems to be strongly supported by the similarity of the rotational barrier for the ethane and the borazane molecules, despite the difference in the electronic structure of the central bond.

Details of the electronic distribution in the molecule can be extracted from the expansion coefficients which yield an orbital description very similar to the previous one [20]. Orbitals $1a_1$ and $2a_1$ are nearly pure $1s$ atomic orbitals of the N and B atoms. Orbital $3a_1$ describes the $2s$ electron of the nitrogen atom, with a small participation of the hydrogen atoms linked to nitrogen. Orbitals $1e$ and $2e$ are responsible for the N–H and B–H bonds built from the $2p_x$ and $2p_y$ orbitals of N or B atoms, and from s orbitals of the H atoms. Orbital $4a_1$ is probably responsible for the B–N bond: it is a bonding orbital built mainly from the $2p_z$ nitrogen orbital together with some $2s$ boron orbital. Quite different is the $5a_1$ orbital, which appears as very delocalized: it has some contribution from the $2s$ and $2p_z$ orbitals of the boron and nitrogen atoms, together with some participation of the hydrogen atoms linked to boron.

The study of the atomic populations indicates negative charges for the N, B, H_B atoms and positive charges for the H_N atoms. In the previous computation [20] the boron atom was almost neutral ($q_B = +0.016$ e) while here its charge is negative ($q_B = -0.159$ e for calculation *A*). This effect is still increased when the $3d$ orbitals are introduced in the basis set ($q_B = -0.171$ e for calculation *B*). A similar increase of the charge with the introduction of $3d$ orbitals has been obtained by Millie [11] in a study of the methyl radical: however, he observed that a further inclusion of p-type orbitals on the hydrogen atoms almost annihilates the effect due to the introduction of $3d$ orbitals on the carbon atom. It might be that the same trend is observed for borazane when some p orbitals are introduced for the hydrogen atoms.

Even with a negative charge on the boron atom, the distribution of the atomic charges is far from the classical formula usually written $B^- \leftarrow N^+$. Nevertheless, there is a total electronic transfer from the NH_3 part to the BH_3 part of the molecule: this transfer amounts to 0.308 e for the staggered conformation. This is in agreement with a polarity $(BH_3)^-$ $(NH_3)^+$. Moreover, from the partition of the atomic populations, one can write the electronic configurations of the boron and nitrogen atoms as:

BH_3NH_3 (staggered)	B: $2s^{0.931}\,2p_x^{0.937}\,2p_y^{0.937}\,2p_z^{0.353}$
	N: $2s^{1.550}\,2p_x^{1.311}\,2p_y^{1.311}\,2p_z^{1.594}$
BH_3	B: $2s^{1.192}\,2p_x^{0.986}\,2p_y^{0.986}\,2p_z^{0.029}$
NH_3	N: $2s^{1.559}\,2p_x^{1.186}\,2p_y^{1.186}\,2p_z^{1.822}$

(we assume that the population of the $1s$ orbitals of the boron and nitrogen atoms in the molecules are equal to 2). From the boron configuration which is very close to sp^2, one will notice the promotion of one $2s$ electron with respect to the atomic configuration s^2p. This appears in the borazane molecule as well as in the BH_3 molecule. Another noticeable feature is the limited amount of electronic transfer from the $2p_z$ orbital of nitrogen to the $2p_z$ orbital of boron, upon molecular formation from the BH_3 and NH_3 molecules. The computed values for the gross atomic populations in BH_3, NH_3 and BH_3NH_3 show that the charges on the boron and nitrogen atoms do not vary appreciably when the borazane molecule is formed. The remarkable change appears for the hydrogen atoms: in BH_3 the H atoms are positively charged but become negative in BH_3NH_3, while the positive charge of the H atoms in NH_3 increases from $+0.27$ e to $+0.36$ e. So the formation of the BH_3NH_3 molecule would imply a strong electronic transfer from the H atoms of NH_3 to the H atoms of BH_3.

From the population analysis, it was found that the overlap population for the B–N bond is surprisingly low. This can be understood if one considers the main terms in the decomposition of this overlap population (Table 10). This shows quite clearly that the 2*s* orbital of boron, which otherwise gives a high contribution to the B–H bonds, does not at all participate to the formation of the N–B bond: the N*s*–B*s* overlap population is a large negative number. The N–B bond is essentially contructed from the $2p_z$ orbital of boron and the 2*s* and $2p_z$ orbitals of nitrogen.

Table 10. *Breakdown of the overlap population for the* B–N *bond*

	BH_3–NH_3	
	Staggered	Eclipsed
N*s*, B*s*	−0.16963	−0.17656
N*s*, B $2p_z$	0.19169	0.19252
N $2p_x$, B $2p_x$	−0.02412	−0.04406
N $2p_z$, B*s*	−0.05385	−0.06312
N $2p_z$, B $2p_z$	0.18305	0.18344

Sections of the total electron densities obtained from the wave-functions are shown in Figs. 1–4. The section plane contains the threefold axis, and one hydrogen atom for BH_3 (Fig. 1) and NH_3 (Fig. 1), or two hydrogen atoms for BH_3NH_3 (Figs. 3 and 4). To study the redistribution of charge which results in the formation of a chemical bond, one usually turns to the density difference maps which are obtained by subtracting from the total molecular density the density distributions of the constituent atoms [17, 18]. Since we are interested in the electronic redistribution upon formation of BH_3NH_3 from BH_3 and NH_3, we rather use difference plots obtained by subtracting the sum of the BH_3 and NH_3 densities from the BH_3NH_3 density (Figs. 4 and 5). They are given only as indicative results: our wavefunction is far from the Hartree-Fock limit, which would insure one-electron density distributions correct to the second order. These plots illustrate the increase of the electronic charge in the B–N bond region, and the decrease near the B and N nuclei. For diatomic molecules [1], a general characteristic of these $\Delta \varrho$ maps is uniformly a build-up of charge between the nuclei and in the region behind the nuclei (away from the bond). For the borazane molecule, there appears to be an increase of the electronic density behind the boron atom, while there is a decrease behind the nitrogen atom. Moreoever, the build-up of charge between the nuclei is shifted towards the boron atom. According to Bader *et al.*, the characteristics of ionic binding can be defined as: (i) a clear-cut transfer of charge from the close proximity of one nucleus to the other, (ii) a polarization of the density increase localized on the anionic nucleus and of the density remaining on the cationic nucleus both in a direction counter to the direction of the charge transfer.

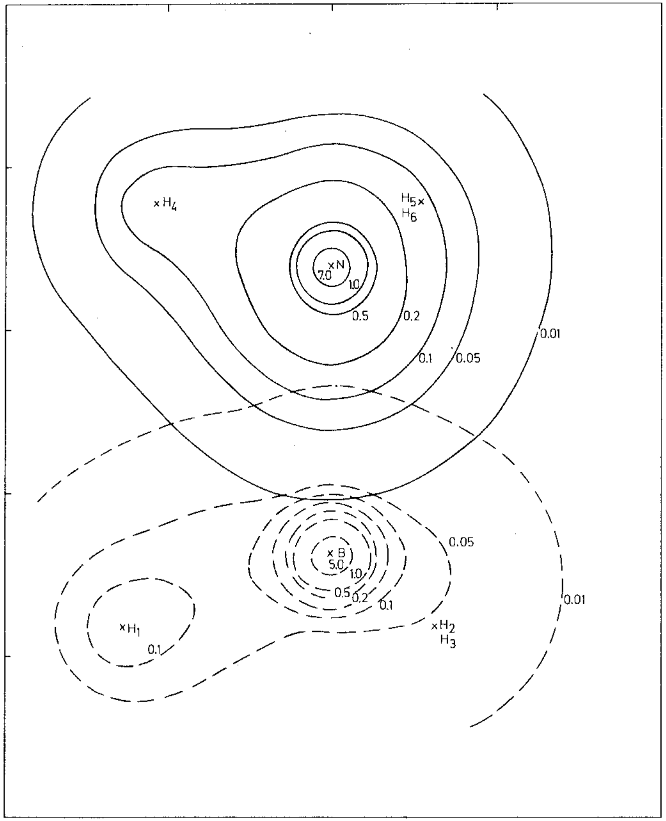

Fig. 1

Total molecular charge density for the NH_3 and the BH_3 molecules

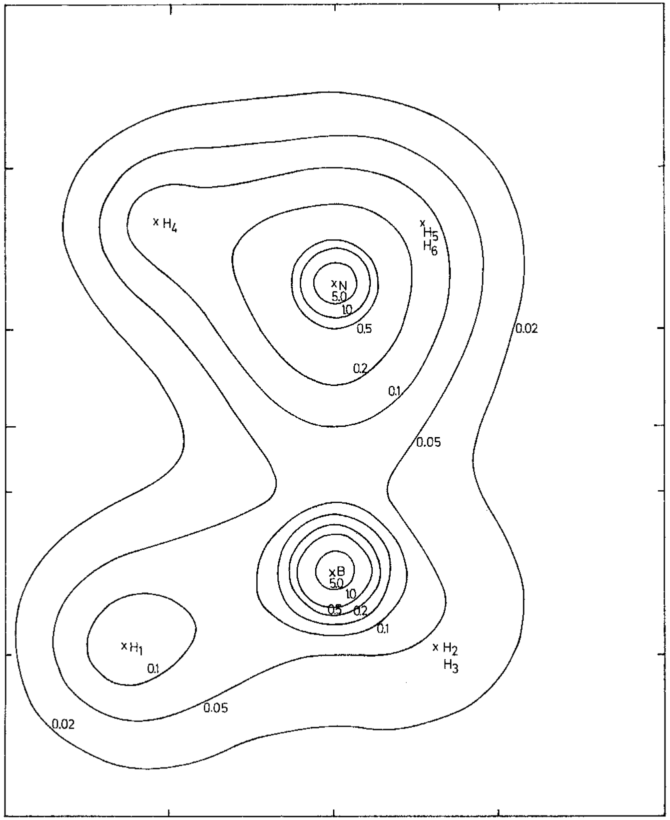

Fig. 2

Total molecular charge density for the BH_3NH_3 molecule
(eclipsed conformation)

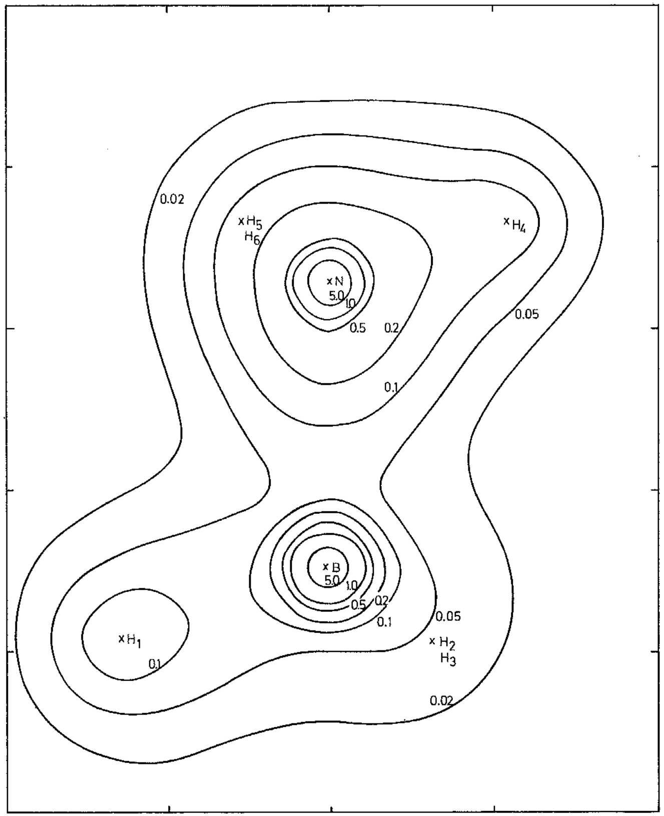

Fig. 3

Total molecular charge density for the BH_3NH_3 molecule (staggered conformation)

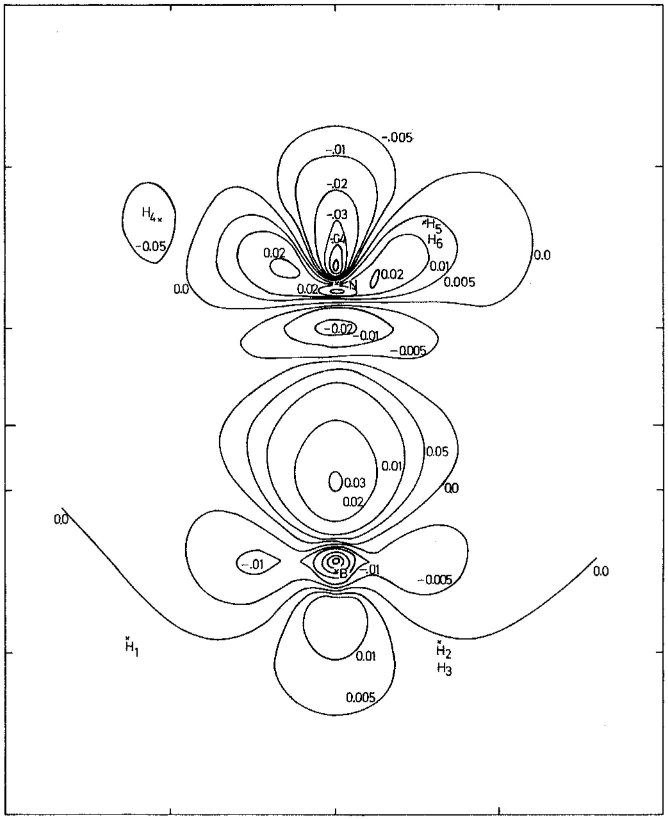

Fig. 4

Density difference map for BH_3NH_3 molecule (eclipsed conformation)

Using these criterion, the binding for the central bond B–N of borazane would be classified as ionic, except for the polarization of the density in the immediate vicinity of the N nucleus. This last criterion could probably be more or less relaxed for molecules of the type AH_m–BH_m: examination of Fig. 5 shows an apparent increase of the electronic density along the B–H bonds, which is probably enough to counterbalance the net force of attraction exerted on the N nucleus by the density transferred to the B atom. A profile of the $\Delta\varrho$ map along the B–N internuclear axis is shown in Fig. 6. One will notice the similarity with the corresponding profile given in Ref. [1] for the LiF molecule, although there is definitely less ionic binding in the borazane molecule.

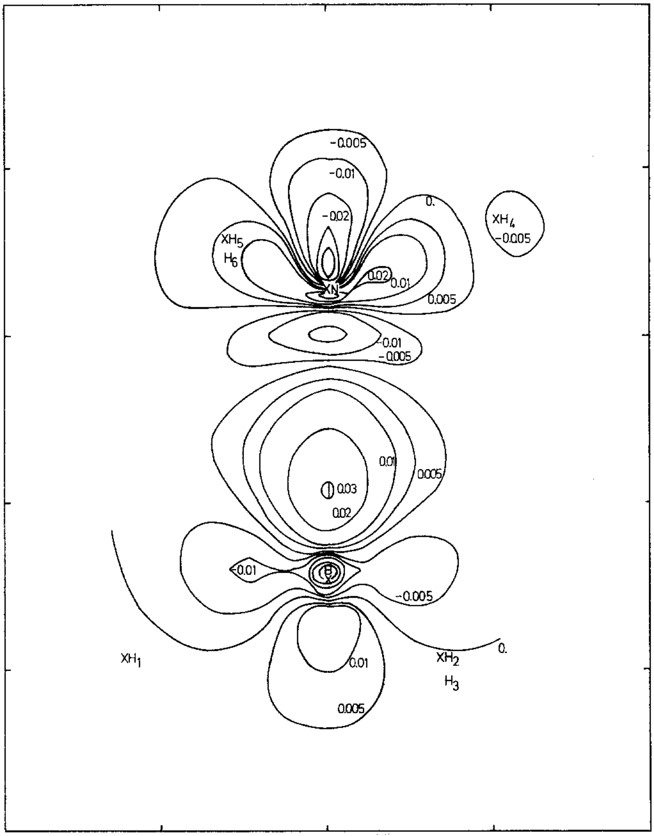

Fig. 5. Density difference map for the BH_3NH_3 molecule (staggered conformation)

From the population analysis, the following conclusions were previously reached: (i) the charges on the boron and nitrogen atoms do not vary appreciably upon molecular formation; (ii) the formal charge on the H atoms of BH_3 becomes negative, (iii) the positive charge of the H atoms in NH_3 is strongly increased. This shows little agreement with the conclusions which one can get from the density difference maps. As already pointed out, examination of the Fig. 5 and the Fig. 6

indicates a strong transfer of charge from the proximity of the nitrogen nucleus to the region surrounding the boron nucleus. One of the hydrogen atoms linked to boron is located in a region where the electronic density is slightly decreased, while in the vicinity of the two others there is probably a slight increase of the electronic density. Moreover, examination of Fig. 5 seems to indicate that there is no variation of the electronic density in the vicinity of the hydrogen nucleus of the NH_3 group. To summarize, the population analysis emphasizes a strong electronic transfer from the H atoms of NH_3 to the H atoms of BH_3, while the density difference maps point to a strong electronic rearrangement in the region of the B–N bond. However, it is clear from this work and from Ref. [20] that any improvement in the basis set used brings some marked variations in the conclusions of the population analysis. We postpone any attempt to clarify the disagreement between the population analysis and the density difference maps, up to the time where wavefunctions close enough to the Hartree-Fock limit are available.

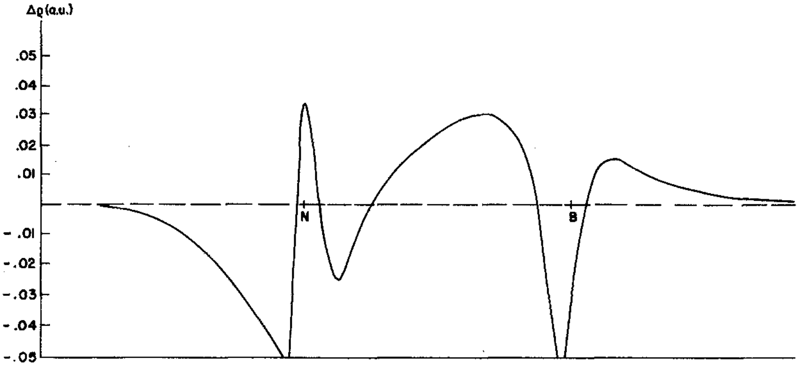

Fig. 6. Density difference distribution along the molecular axis

Acknowledgement. We gratefully acknowledge some support from Prof. R. Daudel during the beginning of this work in Paris. We thank Dr. E. Clementi for making available the program used in the plotting of the density maps.

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Dr. A. Veillard
IBM Corporation
Monterey and Cottle Roads
San José, California 95114, USA