Mechanism of the Curtius-type Rearrangement in the Boron Series. An *Ab Initio* Study of the Borylnitrene (H₂B–N)–Iminoborane (HB=NH) Isomerisation

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Ab initio calculations on the model H_2BN to HBNH rearrangement suggest that the Curtius-type thermolysis of boron azide (R_2B–N_3) yielding iminoborane (RB=NR) does *not* involve the intermediacy of borylnitrene (R_2B–N); under photochemical conditions, the latter can, however, be formed from the lowest-lying triplet state of azide and does *not* rearrange to its more stable isomer but undergoes instead typical reactions.

It is now recognized that the Curtius-type rearrangement (equation 1) is a quite general and effective method for the preparation of imino-compounds (2) in the gas phase or in solution, from group 13 (B), group 14 (C,Si,Ge), and group 15 (P) azides (1).[1] In the boron series (X = B), formation of iminoboranes from a number of alkyl-, aryl-, or amino-substituted boron azides has been reported by Paetzold and co-workers.[2] As in similar compounds, iminoborane can be appreciably stabilized by the bulkiness of its substituents. In fact, a few tris(trimethylsilyl)silyl(imino)boranes, (Me₃Si)₃Si–B=NR, that are quite stable at room temperature, have recently been isolated and characterized.[3]

From a mechanistic point of view, recent experimental[1] and theoretical[4—6] studies indicated that both thermal and photochemical transformations of azides in the carbon[4] and silicon[6] series do *not* involve a nitrene intermediate whereas the latter may intervene in the phosphorus series.[5] This difference of behaviour has been attributed to the fact that the P atom has a lone pair of electrons and accessible d orbitals.[1]

The decomposition pattern of azidoboranes (3) is at variance. In fact, as shown by reactions with trapping agents, borylnitrene (4b) is exclusively formed during their direct photolysis but is only a minor intermediate under thermal conditions (equation 2).[1,2]

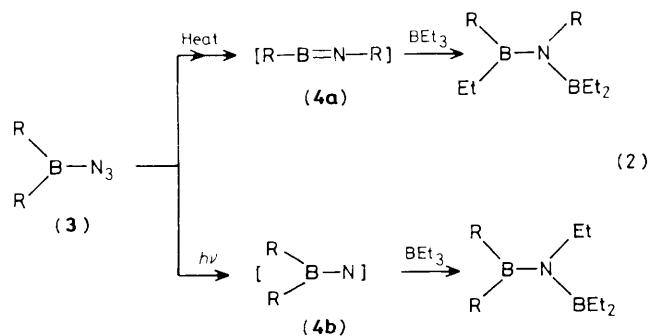In view of the importance of this synthetic route in the preparation of compounds with unusual co-ordination, an
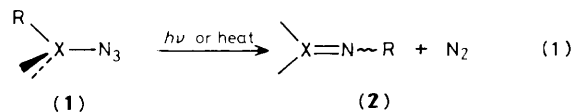
attempt to clarify the role of borylnitrene during the decomposition of azidoboranes has been made by performing *ab initio* molecular orbital calculations on the interconversion of the simplest model species borylnitrene (H_2BN)–iminoborane (HB=NH). The reaction was considered in the lowest singlet and triplet states.

Table 1. Total (a.u.) and zero-point vibrational (Z.P.E., kcal/mol; 1 cal = 4.184 J) energies for [H_2BN] species.

Species[a]	HF/6–31G**[b]	MP4SDTQ/6–31G**[b]	Z.P.E.
³B₂ (5)	−80.17209	−80.39566	14.1
³A′ (6)	−80.07573	−80.33013	11.3
³A (7)	−80.19263	−80.41730	14.2
³A′ (8)	−80.19085	−80.41751	14.0
¹Σ⁺ (9)	−80.29727	−80.57165	17.1
¹A₁ (10)	−80.18848	−80.44288	12.9

[a] Using HF/6–31G*-geometries given in Figure 1. [b] Unrestricted formalism for open-shell species.

X = B, C, Si, Ge, P, P⁺, P=.

∠ HBNH = 44.4°

H 1.189
1.471
B — N
H 119.2

(5) ($^3B_2$)

H₁
1.293 / 1.202
520
B / 1.435
1.188
H 117.4

(6) ($^3A'$)

1.424
1.197 B — N
119.2 125.1 1.004
H H

(7) (^3A)

(v_i 1912i)

1.389
B — N
1.198 0.997
H 117.5 142.6 H

(8) ($^3A'$)

(v_i 489i)

1.223
H — B — N — H
1.167 0.981

(9) ($^1\Sigma^+$)

H 1.188
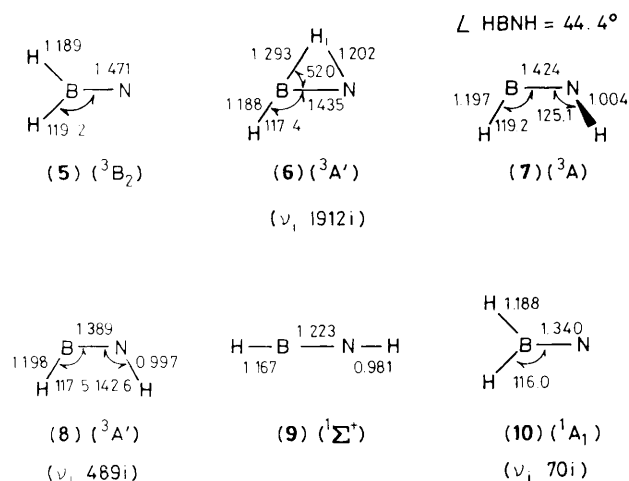1.340
B — N
H 116.0

(10) ($^1A_1$)

(v_i 70i)

Figure 1. HF and UHF/6–31G* optimized geometries for the H_2BN species considered. Bond lengths in Å and bond angles in degrees. v_i: imaginary frequency in cm⁻¹.

Geometrical parameters of the stationary points considered were determined using the force method with analytical gradients and numerical second derivatives (by finite gradient differences)[7] and the 6–31G* basis set[8] (Figure 1). Harmonic vibrational frequencies were calculated at the HF/6–31G* level in order to characterize stationary points as minima or transition structures and to calculate zero-point vibrational contributions to relative energies.

The lowest triplet state of borylnitrene has a planar structure (5) [$^3B_2$ ⋯ (5a₁)¹ (3b₂)¹]. At the UHF/6–31G* level, the cis-skewed conformation (7) is a minimum while the planar (8) has one imaginary frequency (no trans-conformation can be located as a stationary point). Nevertheless, (8) becomes lower in energy than (7) after inclusion of correlation energy (Table 1). The latter was treated via the full fourth-order Møller-Plesset perturbation theory including all single, double, triple, and quadruple excitations (MP4SDTQ)[9] relative to the HF/6–31G** reference configurations. Therefore, it can be concluded that the triplet iminoborane has a cis-planar conformation (8). The transition structure (6) for the 1,2-hydrogen shift linking both triplet minima (5) and (8) has C_s symmetry. The ratio of distances BH_i/NH_i in (6) is comparable to the ratio of the BH and NH distances in (8).

The planar closed-shell singlet borylnitrene (10) ($^1A_1$) is calculated to be a first-order saddle point on the HF/6–31G* energy surface and collapses in fact to the iminoborane (9) following relaxation of symmetry constraint. Geometries and vibrational frequencies of (9) have been examined in previous papers.[10] Recent X-ray studies reported values of 1.22—1.26 Å[2,3] for the B–N distance in substituted iminoboranes. As usual, the calculated wavenumber of 1976 cm⁻¹ for the B–N stretching mode in (9) is 11% larger than the experimental value.[11] We also note that intense bands in the 1875—2030 cm⁻¹ region have been observed in i.r. spectra of substituted iminoboranes and attributed to the B–N stretching mode.

In contrast to the situation in CH_3N,[4] SiH_3N,[6] and PH_3N^+,[5] both singlet structures surprisingly lie lower in energy than the triplet ones so that intersystem crossing cannot occur (Figure 2). Within the two triplet structures, (5) lies 13.8 kcal/mol above (8) but there is a significant energy barrier (38.3 kcal/mol) between them. Accordingly, the triplet borylnitrene
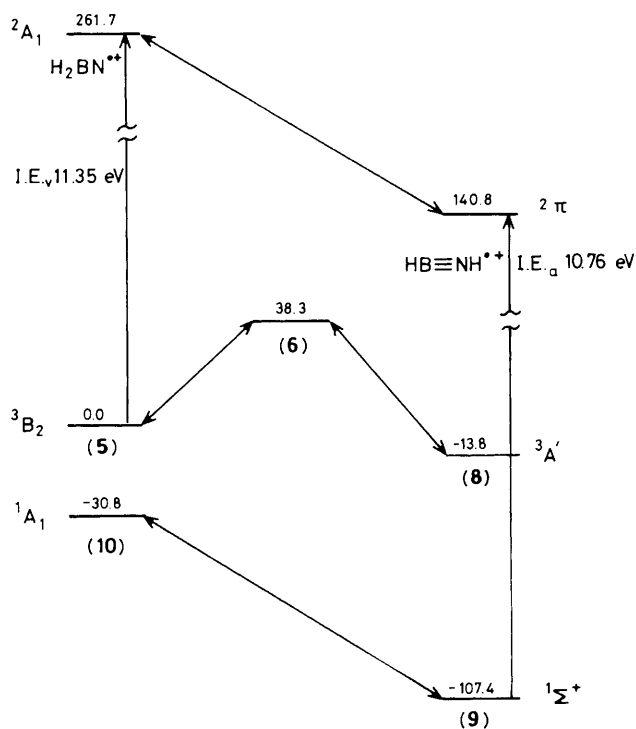
$^2A_1$ 261.7
$H_2BN^{\bullet\bullet}$

I.E.ᵥ 11.35 eV

140.8 2 π
HB≡NH$^{\bullet+}$ I.E.ₐ 10.76 eV

38.3
(6)

$^3B_2$ 0.0
(5)

-13.8 $^3A'$
(8)

$^1A_1$ -30.8
(10)

-107.4 $^1\Sigma^+$
(9)

Figure 2. Schematic energy profile for the H_2BN to HBNH rearrangement. Relative energies [ΔE(MP4) + ΔZPE] are given in kcal/mol (1 cal = 4.184 J). I.E.ᵥ and I.E.ₐ: vertical and adiabatic ionization energies.

(5), if formed during the decomposition of azidoborane, should be stable with respect to unimolecular rearrangement and can undergo typical reactions with trapping agents. This becomes even more likely when H atoms are replaced by alkyl or bulky substituents and thus corroborates well the experimental findings partly given in equation (2).

In this context, the observed photochemical fragmentation of an azidoborane (3) [yielding (4b)] should occur in its triplet excited state. Such behaviour differs from that of silylazides ($R_3Si–N_3$) or azidophosphonium salts ($R_3PN^+ \cdot X^-$) whose direct photolysis has been shown to occur in their singlet ground states.[1,5—6] Further calculations on molecular and electronic structures of corresponding azides are necessary to clarify this difference. With regard to the thermal process, Figure 2 also suggests that nitrene does not participate in the thermolysis of (3) leading to the singlet iminoborane (4a). As in previous cases (H_3CN, H_3SiN, H_3PN^+),[4—6] the concerted substituent migration–nitrogen loss mechanism from the singlet azide appears to be plausible.

In summary, a major conclusion can be drawn from this preliminary work: the thermolysis of boron azide does not involve borylnitrene as a discrete intermediate. The latter can however be photochemically generated from the triplet azide and should be stable with respect to unimolecular rearrangement.

Finally, in order to gain further information on the electronic structure of species considered, their ionization energies have also been calculated and are given in Figure 2. We note that the borylnitrene radical cation $H_2BN^{\bullet+}$ undergoes barrier-free rearrangement to the stable form $HBNH^{\bullet+}$ which also has a linear structure.

All calculations were carried out on the facilities of the Computer Centre, University College, Dublin, Eire. Dr. Guy Bertrand (Toulouse) is gratefully acknowledged for stimulating correspondence.

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