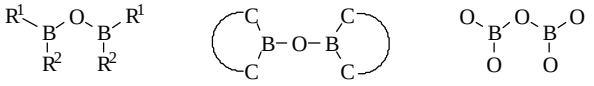
A theoretical study of internal rotation in H_2BOBH_2 and $H_2BNBH_2^-$

Ruslan M. Minyaev* and Evgenii A. Lepin

Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 863 228 5667

It has been shown by using MP2(fc)/6-31G** and MP2(fc)/6-311+ +G** methods that the internal rotation of $H_2BNBH_2^-$ and H_2BOBH_2 allene structures occurs through the corresponding angle structures with a very small energy barrier.

Boron anhydrides **1**, according to experimental data,[1–3] have a stable angular structure with bond angle BOB varying in a wide range depending on R^1, R^2.



1 **2** **3**

The BOB fragment in anhydrides **2** appears[3,4] to have a linear structure. The angle form of the BOB fragment (BOB < 180°) has been observed in pyroborate ions **3** of various metal salts.[3] The planar structure (D_{2h}) has been established for **1** ($R^1 = R^2 = F$).[5] At the same time, according to X-ray data,[6,7] 'isoelectronic (relative to BOB fragment) analogues' **4** and **5** have the allene structure.

4 **5**

Bond BO is considered to be stronger than BC and BN bonds and to have higher π-bond order.[3] Hence these facts should lead to more favourable stable form of the allene type for **1**–**4**. To elucidate the thermodynamic difference between allene and angle forms of the BOB and BNB fragments in **1**–**5** here we report *ab initio* MP2(fc)/6-31G** and MP2(fc)/6-311+ +G**[8,9] calculations on the thermodynamic stability of allene **6** and angle **7** structures and their rearrangements (internal rotation) for model compounds H_2BYBH_2 (Y = N^-, O).

6, C_{2v} **7**, D_{2d}

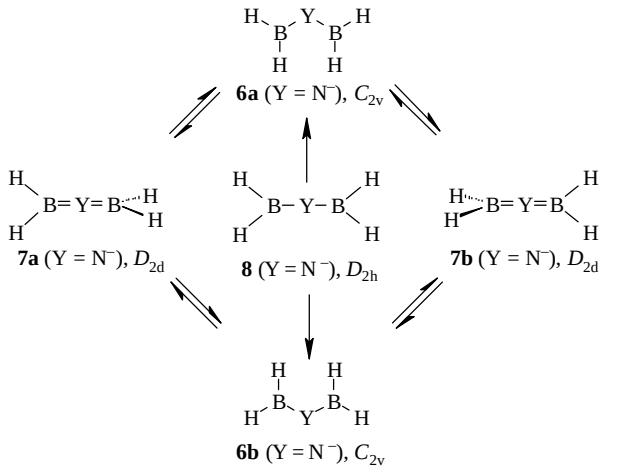
Allene structure (**7**, Y = N^-), according to *ab initio* calculations, corresponds to a minimum on the H_2BNBH_2 potential energy surface (PES) whereas the angle form (**6**, Y = N^-) corresponds to a saddle point (hessian has one negative eigenvalue) and is the transition state structure for simultaneous internal rotation of the both BH_2 groups around BN bonds (Scheme 1).

Bond BN predicted by *ab initio* calculations (Figure 1) in **7** is very close to the similar bond in **5** where it equals 1.38(2) Å.[7] Planar structure (**8**, Y = N^-) with D_{2h} symmetry corresponds to the top of a hill (hessian has two negative eigenvalues). Geometry and energy for **6**–**8** are presented in Figure 1 and Table 1.

Thus, anion $(H_2B)_2N^-$ is stable only in the allene form (**7**, Y = N^-) and internal rotation in **7** occurs, according to Scheme 1, by two equivalent pathways **7a** ⇌ **6a** ⇌ **7b** and **7a** ⇌ **6b** ⇌ **7b**, with overcoming of the energy barrier of 15.5 and 12.8 kcal mol^{-1}† predicted by MP2(fc)/6-31G** and MP2(fc)/6-311+ +G** methods, respectively. In contrast to anion $(H_2B)_2N^-$, boran $(H_2B)_2O$ has two stable structures, angle **6** and allene **7**, the energy difference of which is very small. The *ab initio* MP2(fc)/6-31G** method predicts that allene form **7** is more favourable by 0.43 kcal mol^{-1} than angle structure **6**. Increasing the level of calculation to MP2(fc)/6-311+ +G** changes the energetic stability of **6** and **7**: angle structure **6** becomes 1.3 kcal mol^{-1} more favourable than **7**. Both structures **6** and **7** can convert into each other *via* transition state structure **9** by overcoming energy barrier of 1 and 0.2 kcal mol^{-1} calculated by MP2(fc)/6-31G** and MP2(fc)/6-311+ +G** methods, respectively (see Table 1). Geometric and energetic characteristics of **6**–**9** are presented in Table 1 and Figure 2. The length of the BO bond predicted by *ab initio* calculations is in the range of experimentally-known lengths (1.30–1.40 Å) of similar bonds.[1–5,10]

The PES topology of $(H_2B)_2Y$ (Y = N^-, O) in the region of the internal rotation, according to *ab initio* calculations, is very complicated and internal rotation in $(H_2B)_2Y$ which occurs due to Scheme 1 differs from the usual one-valley pathway. To

† 1 cal=4.184 J.



Scheme 1

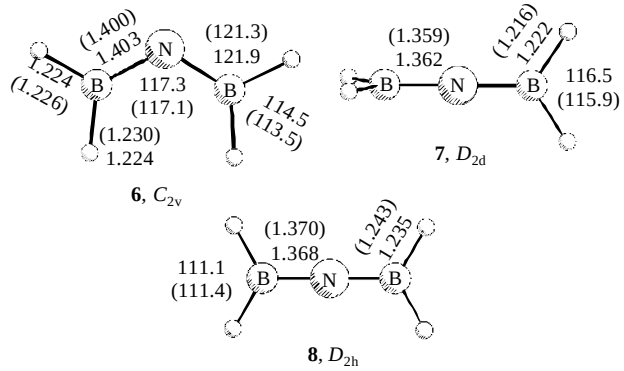


Figure 1 Geometric parameters of stable structure **7**, transition state structure **6** and the configuration **8** corresponding to stationary point with index two for $(H_2B)_2N^-$ calculated by *ab initio* MP2(fc)/6-31G** and MP2(fc)/6-311+ +G** (number in parenthesis). Bond lengths are given in angstrom, bond angle in degrees.

Table 1 Total energy (E_{tot} in hartree), relative energy (ΔE in kcal mol^{-1}),[a] the number of the negative hessian eigenvalues (λ), zero point energy (ZPE in hartree), relative energy with including ZPE (ΔE_{ZPE} in kcal mol^{-1}),[a] the imaginary or the smallest positive frequency ($i\nu/\nu_1$ in cm^{-1}) predicted by MP2(fc)/6-31G** and MP2(fc)/6-311+ +G** (in parenthesis) methods for structures **6**–**9** of H_2BYBH_2 (Y = N$^-$, O).

Structure	E_{tot}	ΔE	λ	ZPE	ΔE_{ZPE}	$i\nu/\nu_1$
6 (Y = N$^-$), C_{2v}	–106.51136 (–106.57030)	16.5 (12.6)	1 (1)	0.04507 (0.04357)	15.4 (11.8)	i136.5 (i87.8)
7 (Y = N$^-$), D_{2d}	–106.53765 (–106.59043)	0 (0)	0 (0)	0.04674 (0.04492)	0 (0)	257.0 (224.3)
8 (Y = N$^-$), D_{2h}	–106.49421 (–106.54802)	27.2 (26.6)	2 (2)	0.04393 (0.04182)	25.5 (24.6)	i988.3; i262.8 (i964.2; i309.1)
6 (Y = O), C_{2v}	–126.97325 (–127.02904)	0.43 (–1.3)	0 (0)	0.04834 (0.04714)	0.5 (–1.2)	206.4 (214.9)
7 (Y = O), D_{2d}	–126.97394 (–127.02690)	0 (0)	0 (0)	0.04823 (0.04688)	0 (0)	121.3 (92.9)
8 (Y = O), D_{2h}	–126.95743 (–127.01048)	10.4 (10.3)	2 (2)	0.04671 (0.04531)	9.4 (9.3)	i495.7; i284.4 (i492.6; i306.3)
9 (Y = O), C_2	–126.97169 (–127.02651)	1.4 (0.2)	1 (1)	0.04783 (0.04660)	1.2 (0.1)	i180.1 (i95.1)

[a] 1hartree=627.5095 kcalmol^{-1}.

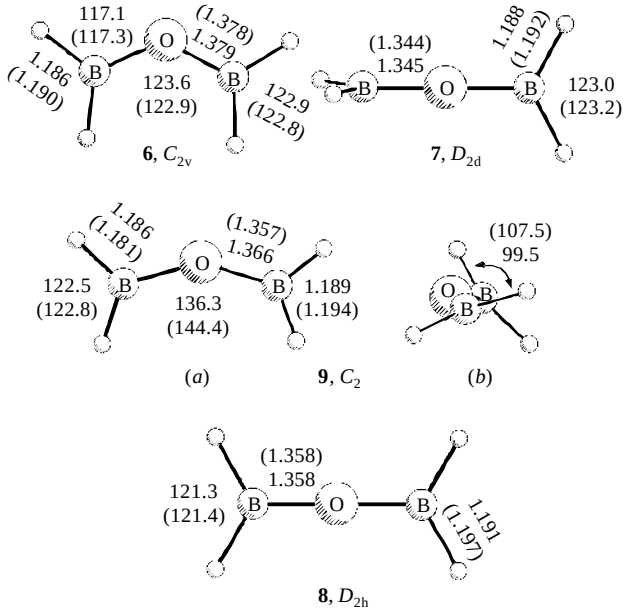


Figure 2 Geometric parameters of stable structures **6** and **7**, transition state structure **9** [in two projections, (*a*) face view and (*b*) side view] and the form **8** corresponding to stationary point with index two for borane $(H_2B)_2O$ calculated by *ab initio* MP2(fc)/6-31G** and MP2(fc)/6-311++G** (number in parenthesis). Bond lengths are given in angstrom, bond angle in degrees.

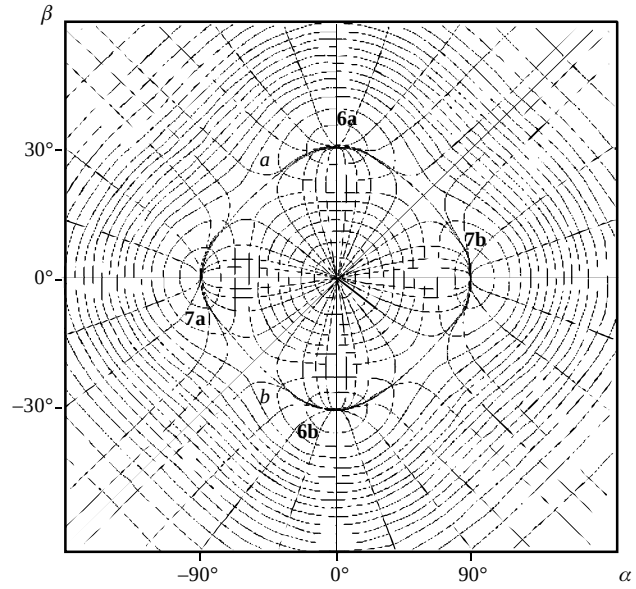


Figure 3 Two-dimensional map and orthogonal trajectories of $V(\alpha,\beta)$. Thin close lines designate contour lines, thin lines being orthogonal to contour lines are gradient lines (orthogonal trajectories). Gradient line reaction path of the internal rotation consists of two equivalent gradient lines *a* and *b*. Angles α denote the rotation angle around OB bond (zero value corresponds to planar structure **8**), β – inversion angle BOB (zero value corresponds to BOB=180°), respectively.

show that the reaction pathway in $(H_2B)_2Y$ consists of two equivalent gradient lines we calculated all gradient lines (orthogonal trajectories) for analytic function $V(\alpha,\beta)$ (where α is a rotational angle and β an inversion angle) approximating the $(H_2B)_2O$ PES in the region of the internal rotation (α = –90 to 90°, β = –90 to +90°). A two-dimensional map of $V(\alpha,\beta)$ and its field of the orthogonal trajectories are presented in Figure 3.

As one can see from Figure 3, all gradient lines are originated or terminated only stationary points ($\Delta E = 0$) or comes to infinity.[11] Gradient lines cannot bifurcate or disappear in regular points ($\Delta E \neq 0$). Only two gradient lines connect minima **7a** and **7b** passing through saddle points **9a**–**d** and 'intermediates' **6a** and **6b**, respectively. These two equivalent gradient lines make up the gradient reaction path of the internal rotation.[11]

Thus, the internal rotation in boranes $(H_2B)_2N^-$ and $(H_2B)_2O$ occurs according to Scheme 1. Small energy difference between the two structures **6** (Y = O) and **7** (Y = O) and the negligible energy barrier separating these forms appears to be crucial in hampering the experimental observation of the separate allene and angle structures.

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