Mechanisms of inversion of bond configuration at the tetrahedral boron atom in five-membered chelate cycles

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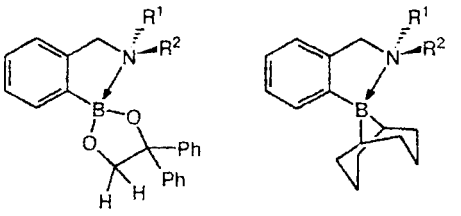
Mechanisms of inversion of the bond configuration at the tetrahedral boron center in five-membered chelate cycles of the 1,3,2-oxazaborolidine and 1,3,2-oxazaborolidene molecules were studied by the *ab initio* MP2(full)/6-31G** method. It was shown that enantiotopomerization occurs by a dissociative mechanism with the cleavage of the B←N bond and the formation of acyclic intermediates with tricoordinate planar boron atom. The calculated energy barriers to inversion of tetrahedral bond configurations at boron centers in the two chelate complexes are equal to 13.1 and 15.4 kcal mol^{-1}, respectively. In contrast to 1,3,2-oxazaborolidine, internal rotation about the B—O bond in its unsaturated analog makes an appreciable contribution to the reaction coordinate.

Key words: *ab initio* calculations, enantiomerization, enantiotopomerization, reaction pathway, 1,3,2-oxazaborolidine, 1,3,2-oxazaborolidene.

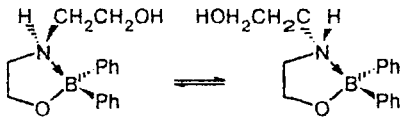
Studies of enantiomerization mechanisms of tetracoordinate tetrahedral bond configurations at the atoms of main group elements including boron atom are important for understanding the nature of chiral purity of biological systems.[1] According to dynamic NMR data, the energy barriers to enantiomerization or enantiotopomerization of intracomplex boron compounds with the coordination N→B bond are relatively low (12 to 24 kcal mol^{-1}).[2] Two mechanisms of intramolecular stereoizomerization, a polytopal rearrangement without a bond cleavage, occurring with the formation of a structure with a planar bond configuration at the tetracoordinate boron atom, and isomerization by a dissociative mechanism with the cleavage of the boron—ligand bond, occurring with the formation of a structure with a planar bond configuration at the tricoordinate boron atom, were considered for the explanation of experimental data.[2—6] Early MNDO[3] and *ab initio*[4,5] calculations showed that the energy of the structure with a planar (or pyramidal) bond configuration at the tetracoordinate boron atom is about 100 kcal mol^{-1} higher than that of a structure with the tetrahedral bond configuration at the same type of boron atom and, hence, the pathway of the reaction of inversion of tetrahedral bond configuration at the boron atom cannot pass through the latter structure since the above value is much larger than the energies of B←N and B—O bonds.[7,8] Thus, the available theoretical and experimental data indicate that stereoizomerization of the boron tetrahedron in boron-containing compounds occurs by a dissociative mechanism with the cleavage of the boron—ligand bond.



1 **2**

$R^1 = R^2$ = Me, Et

Moreover, the heights of the energy barriers to the inversion **3a** ⟹ **3b** of tetrahedral bond configuration at the boron atom in the 1,3,2-oxazaborolidine ring of compound **3** (14.7±0.3 kcal mol^{-1})[9] as well as the heights of the barriers to enantiotopomerization of the tetracoordinate boron atom and to inversion of pyramidalized bond configuration at the nitrogen atom in the intramolecular boron-nitrogen complexes **1** and **2** (11.5 to 14.1 kcal mol^{-1})[10,11] obtained using dynamic ^{1}H and ^{13}C NMR spectroscopy are close to the value of 12.9 kcal mol^{-1} found for the barrier to the B←N bond dissociation in the borane trimethylamine complex,[12] which indicates that this stage is the limiting stage of enantiotopomerization.



3a **3b**

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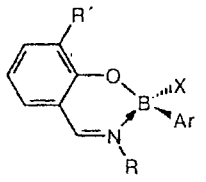
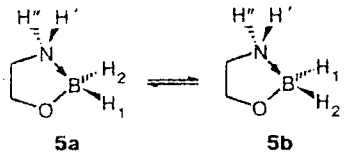
In a number of works[11,13] dedicated to studying the kinetics and mechanism of enantiomerization of the type **4** chiral chelate complexes of tetracoordinate boron it has been pointed out that using dynamic NMR, it is possible to detect two stages of the process separately: the first stage associated with the dissociation of the N→B bond, and the second stage associated with hindered rotation (about C—N or B—C bonds in compounds of the type **1** or about the B—O bond in compounds of the type **4** with R′ = CH=NR) in the intermediate being formed.

In this case rotation about the B—O bond in compounds **4** requires additional expenditure of energy (10 kcal mol^{-1} and more).[13] However, it remains unclear whether the processes mentioned above are kinetically individual stages of a multistage stereoizomerization or they occur concertedly *via* a common transition state. No detailed description of the stereoizomerization mechanism was reported and no transition state structures corresponding to inversion of the bond configuration at the tetrahedral boron atom were found in earlier theoretical studies.[3,4]

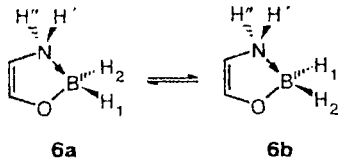


4

X = Ar, OAlk
R = $CHMe_2$, CH_2Ph, Ar
R′ = H, CH=NR



5a **5b**



6a **6b**

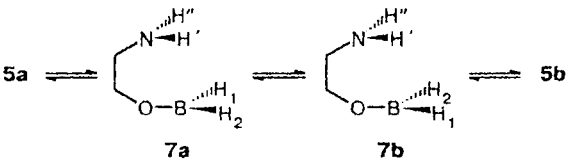
The aim of this work was to perform a detailed study of the mechanism and energetics of the stereoisomerizations **5a** ⟹ **5b** and **6a** ⟹ **6b** in the chelate complexes **5** and **6** containing tetracoordinate boron atoms using *ab initio* (MP2(full)/6-31G**)[14] calculations. These complexes simulate corresponding experimentally studied systems[2] in which the tetrahedral boron atom is a constituent of saturated and unsaturated cycles.

Procedure for calculations

Ab initio calculations were carried out by the restricted Hartree—Fock (RHF) method with inclusion of correlation energy for all (both valence and core) electrons at the second-order Møller—Plesset level (MP2(full)) of perturbation theory in the split-valence 6-31G(d,p) basis set using the GAUSSIAN-94 [24] and GAMESS [25] programs on RISC-6000 and DEC Alphastation 500 workstations. Full optimization of the geometry of the molecular structures corresponding to the saddle points (λ = 1, hereinafter λ is the number of negative eigenvalues of the Hesse matrix at a given stationary point[15]) and to the energy minima (λ = 0) on the potential energy surface (PES) was carried out up to a gradient value of 10^{-5} Hartree/Bohr. The structures corresponding to energy minima on the PES were obtained by the method of steepest descent (by moving along the gradient line) from the saddle point (transition state) to the neighboring stationary point (a saddle point or a minimum). This method makes it possible to find a correct gradient reaction pathway[15] connecting the minima to corresponding saddle points. The initial direction of the gradient line was specified by minor displacement (1/100 of the value of the normalized transition vector) along the direction of the transition vector. Graphic images of the molecular structures were obtained using the MOLDEN program[26] for which Cartesian atomic coordinates of corresponding molecules taken at the final step of *ab initio* calculations served as input parameters.

Results and Discussion

Mechanism of enantiotopomerization in 1,3,2-oxazaborolidine. The results of *ab initio* calculations show that two isomeric structures, the cyclic structure **5** with the tetrahedrally coordinate boron atom and the open 2-aminoethyl diphenylborinate type structure **7** with a planar bond configuration at the tricoordinate boron atom, correspond to the energy minimum (λ = 0) on the PES.



5a **7a** **7b** **5b**

The calculated energy and geometric parameters of these structures are listed in Table 1 and shown in Fig. 1.

The cyclic structure **5** is nonplanar (the N—C—C—O dihedral angle is 40°) and has a half-chair conformation. From comparison with the results of X-ray study of 2-aminoethyl diphenylborinate[16] also shown in Fig. 1 (figures in parentheses) it follows that the theoretical data agree well with the experimental data. However, the B←N bond (1.717 Å) predicted by the *ab initio* calculations is somewhat lengthened as compared with the corresponding experimental value for the diphenyl derivative. At the same time, it lies within the limits of the known[17,18] lengths of donor-acceptor (dative[19]) B←N bonds and is close to the lengths of analogous bonds in borane ammonia complex (H_3BNH_3) and borane trimethylamine complex (1.658(1) and 1.70±0.01 Å, respectively)*. In addition, the detailed theoretical study of the donor-acceptor B←N bond in the borane monoammoniate

* Microwave spectroscopy data (Refs. 20 and 21, respectively).

Table 1. Energy parameters of structures **5**—**9** and **14** calculated by the *ab initio* MP2(full)/6-31G** method

Structure	E_{tot}	ΔE	λ	ZPE	ΔH	iv/v_1, v_2
5	−235.18515	0	0	0.11668	0	139; 325
7	−235.17199	8.26	0	0.11391	−7.33	82; 150
8	−235.16430	13.08	1	0.11253	−11.23	*i*689.8
6	−233.97671	0	0	0.09160	0	124; 445
9	−233.96145	9.57	0	0.08850	−8.43	107; 193
14	−233.95218	15.39	1	0.08812	−13.58	*i*200.3

Note. All systems have C_1 symmetry. E_{tot}/au is the total energy (1 au = 627.5095 kcal mol^{-1}); ΔE/kcal mol^{-1} is the relative energy, λ is the number of negative eigenvalues of the Hessian; ZPE/au is the zero-point vibrational energy; ΔH/kcal mol^{-1} is the relative enthalpy under standard conditions, T = 298.15 K and p = 1 atm); v_1 and v_2 (in cm^{-1}) are the lowest frequencies of normal vibrations; and iv/cm^{-1} is the imaginary frequency.

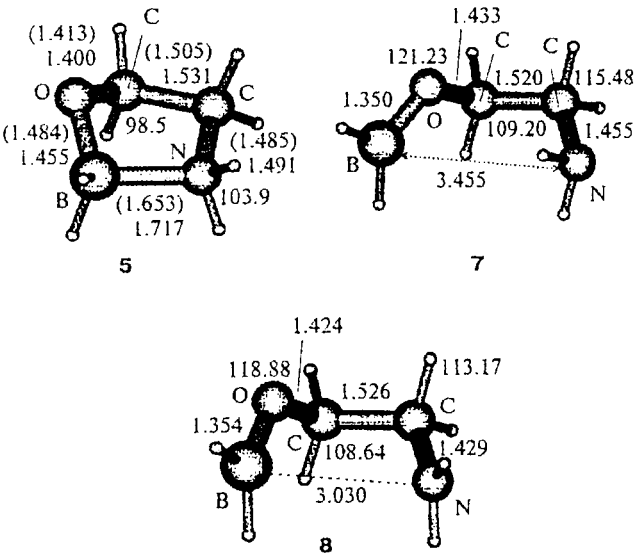


Fig. 1. Geometric parameters of 1,3,2-oxazaborolidine **5** (λ = 0), intermediate **7** (λ = 0), and transition state **8** (λ = 1) calculated method MP2(full)/6-31G**. Bond lengths are given in Å and bond angles are given in degrees; all systems have C_1 symmetry. For structure **5**, data of X-ray study of 2-aminoethyl diphenylborinate[16] are given in parentheses.

molecule by different *ab initio* methods[22] showed that the length of the B←N bond predicted by the MP2(full)/6-31G** method (1.661 Å) is in very good agreement with the experimental value.[20] Therefore, one can expect that calculations using the above method performed in this study reproduce adequately the values of geometric parameters of the compounds studied.

According to calculations, the open structure **7** corresponding to a minimum on the PES (λ = 0) is 8.3 kcal mol^{-1} less stable than the cyclic form **5**. The lowest frequency of normal vibration for structure **7** is positive (only 82 cm^{-1}), which indicates that this structure is stereochemically labile. Both hydrogen atoms bonded to the nitrogen atom are oriented towards hydrogen atoms bonded to the boron atom. This is likely due to a weak electrostatic interaction between these atoms (weak H—H interaction[23]): each H atom bonded to the nitrogen atom has a positive charge of 0.300 au, while each H atom bonded to the boron atom has a negative charge of −0.120 au.

The structure **8** (see Fig. 1) corresponds to a saddle point (λ = 1) on the PES and is a true transition state between the cyclic and acyclic forms (**5** and **7**, respectively). This conclusion is confirmed by the calculations of the continuous gradient line reaction pathway[15] from point **8** to both minima **5** and **7** along the line of steepest descent, according to which the ring opening **5**→**7** occurs with overcoming of an energy barrier of 13.1 kcal mol^{-1}. The energy profile of the process and the evolution of the structure when moving along this pathway are shown in Fig. 2. Except for the angle of bond pyramidalization at the nitrogen atom and the B...N distance, which for the form **8** is 0.4 Å shorter than for structure **7**, almost all geometric parameters of the structure **8** are rather close to corresponding values for the acyclic form **7**.

The experimentally observed enantiomerization **3a** ⇌ **3b** can occur as a result of exchange of ligand positions at the boron atom or at the nitrogen atom. In the model compound **5**, exchange of the positions of hydrogen atoms at the boron atom involving the formation of intermediate **7** can occur by further low-energy internal rotation about the O—C, C—C, or C—N bonds in the latter compound. We failed to localize transition states for internal rotations. However, structures corresponding to different local minima near **7** with energies 2—7 kcal mol^{-1} higher than that of form **7** were found. It should be noted that the fact that the rotation about the B—O bond is somewhat hindered as compared to rotations about other bonds is due to the high degree of double bonding for this bond in the acyclic form: the Mulliken orders of the B—O bonds in structures **5** and **7** are equal to 0.886 and 1.261, respectively. Therefore, rotation about this bond can not play a determining role in the enantiotopomerization. At the same time, the above internal rotations make no appreciable contributions to the barrier to enantiotopomerization. For instance, rotation about the C—N bond occurs with overcoming of a barrier not higher than 2 kcal mol^{-1}, which is in agreement with the height of the overall barrier to enantiotopomerization (13.1 kcal mol^{-1}). According to calculations, the rate constant for enantiotopomerization must be equal to the halved rate constant of the B←N bond dissociation in the cyclic form.

This, according to our *ab initio* calculations, the enantiotopomerization **5a** ⇌ **5b** occurs with the cleavage of the B←N bond and the formation of intermediate acyclic structure followed by internal rotation of ligands. The predicted energy barrier (13.1 kcal mol^{-1}) is in good agreement with the experimental value for isomerization **3a** ⇌ **3b** (14.7 kcal mol^{-1}) and with the conclusion

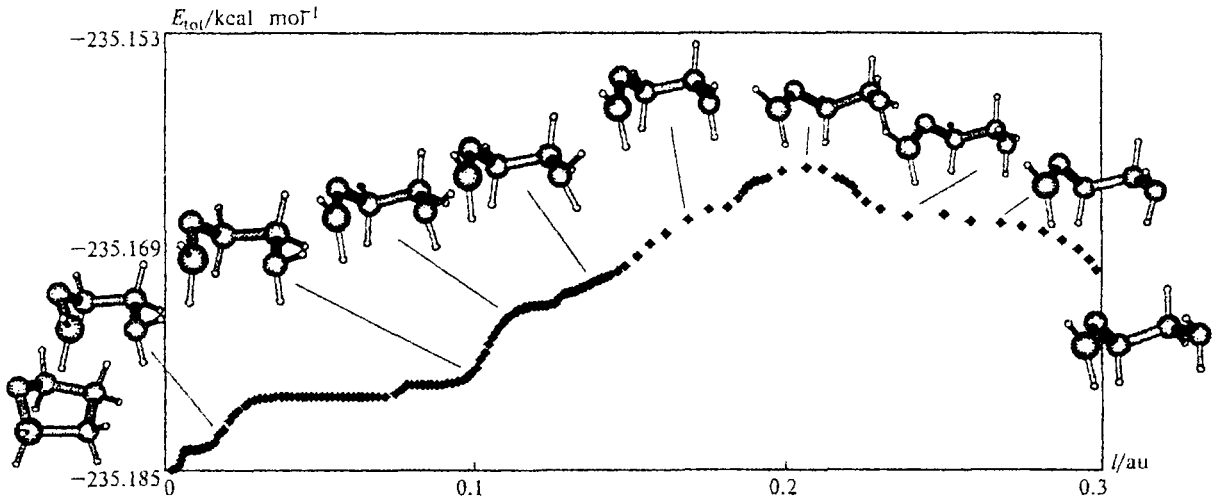
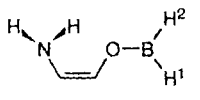


Fig. 2. Energy profile of the PES along the pathway of ring opening 5→7 and the evolution of the molecular structure along this pathway calculated by the MP2(full)/6-31G** method. *l* is the shift along the gradient line reaction pathway; the origin corresponds to structure 5.

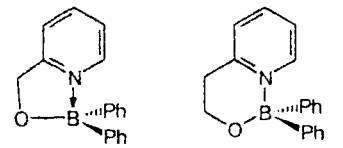
that the stage of the B←N bond dissociation in chelates **3**—**6** makes the major contribution to the heights of the barriers to enantiotopomerization and enantiomerization.

Mechanism of enantiotopomerization in 1,3,2-oxazaborolidene. According to *ab initio* calculations, both cyclic structure **6** and acyclic structure **9** of this boron complex correspond to energy minima on the PES (λ = 0). The calculated energy and geometric parameters of these structures are listed in Table 1 and shown in Fig. 3, respectively.



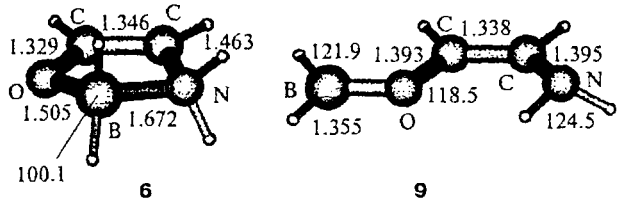
9

The cyclic structure **6** predicted by calculations has a nearly planar ring. The boron atom slightly deviates from the plane passing through the OCCN atoms (the C—C—O—B dihedral angle is 10°). However, a structure with C_s symmetry and planar five-membered ring is a saddle point on PES (λ = 1) and corresponds to transition state of inversion of the five-membered cycle with a low energy barrier (0.1 kcal mol^{-1}), which indicates a very high degree of structural flexibility of the cyclic system. According to calculations, the length of the B←N bond is 1.672 Å, which is somewhat shorter than that in 1,3,2-oxazaborolidine **5** and is very close to the lengths of the B←N bonds in borane ammonia complexes[17,19—21] and recently obtained diphenyl(2-pyridylmethoxy-*O*,*N*)borane **10** (1.642 Å) and diphenyl[2-(2-pyridyl)ethoxy-*O*,*N*]borane **11** (1.685 Å).[18] It is noteworthy that the B—O bond in structure **6** is appreciably lengthened as compared with **5**, which is likely due to delocalization of electrons in the conjugated system, strengthening of the B←N bond, and weakening of the B—O bond.

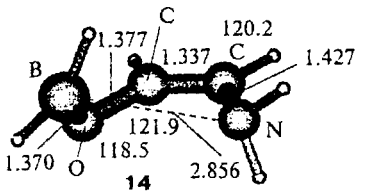


10 **11**

According to calculations, acyclic structure **9** is 9.6 kcal mol^{-1} less thermodynamically stable than cyclic form **6** and the lowest frequency of normal vibration for **9** is 107.3 cm^{-1}. In structure **9**, all atoms except



6 **9**



14

Fig. 3. Geometric parameters 1,3,2-oxazaborolidene **6** (λ = 0), intermediate **9** (λ = 0), and transition state **14** (λ = 1), calculated method MP2(full)/6-31G**. Bond lengths are given in Å and bond angles are given in degrees; all systems have C_1 symmetry.

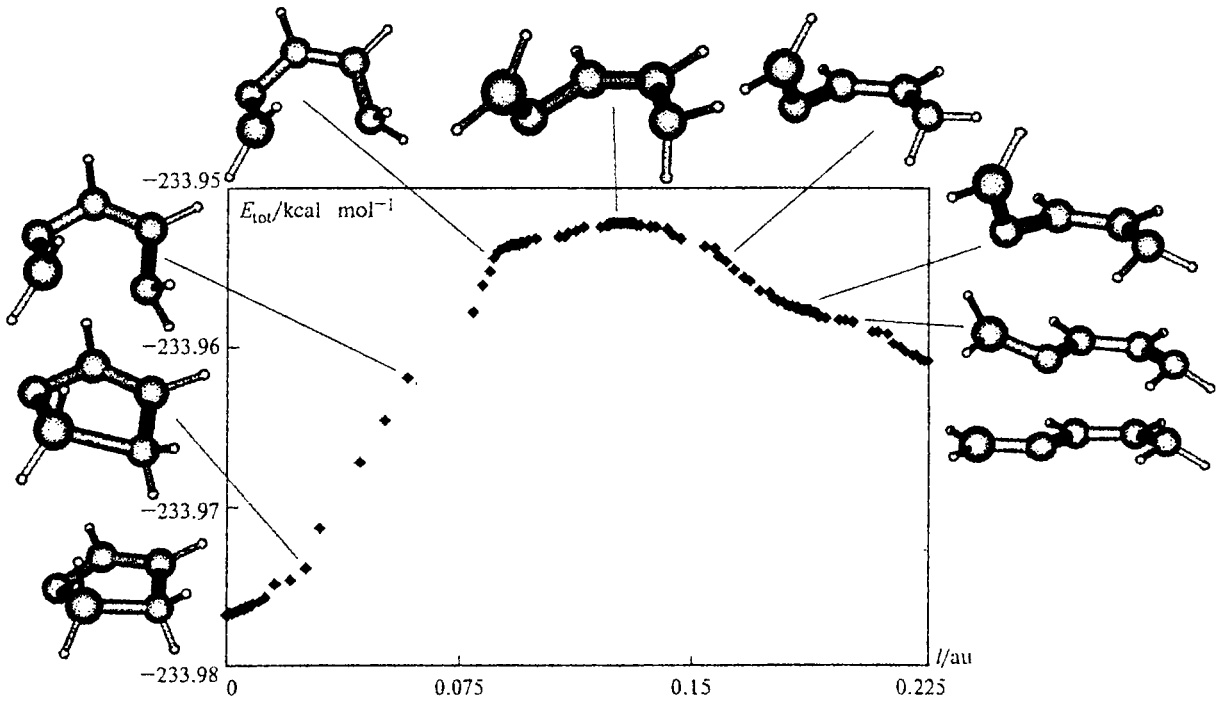
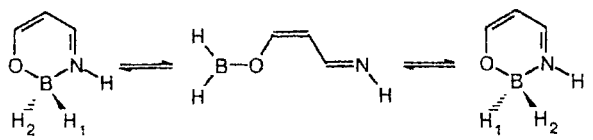


Fig. 4. Energy profile of the PES along the pathway of ring opening **6**→**9** system and the evolution of the molecular structure along this pathway calculated by the MP2(full)/6-31G** method. *l* is the shift along the gradient line reaction pathway; the origin corresponds to structure **6**.

for H atoms at the pyramidalized nitrogen atom, lie in the same plane. Inversion of N—H bonds occurs with the formation of intermediate planar structure with C_s symmetry with an energy barrier not higher than 2 kcal mol^{-1}. It should be noted that the assumption of the possibility for acyclic structure **13** to exist as intermediate on the pathway of enantiomerization of chelates **12** simulating experimentally studied systems **4** was first time proposed on the basis of MNDO calculations.[3]



12a **13** **12b**

However, no transition state was found on the pathway **12** ⟷ **13**, the pathway of the enantiotopomerization has not been investigated, and the nature of stationary points using calculations of the Hesse matrix has not been studied earlier.[3]

According to our *ab initio* calculations, structure **14** (see Fig. 3) corresponds to a saddle point on the PES (λ = 1) and is a true transition state between the cyclic structure **6** and acyclic structure **9**. This conclusion was confirmed by calculations of a continuous reaction pathway issuing out of the saddle point **14** along both directions of the transition vector and arriving at both minima **6** and **9** along the steepest descent direction. The energy profile of the process and the evolution of the system along this pathway are shown in Fig. 4.

Unlike transition state **8**, geometric parameters of the transition state **14** are intermediate between the corresponding values for structures **6** and **9**. The calculations predict that the B...N distance in structure **14** is much shorter than in **8**. In the first case, almost no rotation of terminal BH_2 and NH_2 groups about the B—O and N—C bond, respectively, occurs in the course of the ring opening **5**→**7**. However, in the case of 1,3,2-oxazaborolidene, these groups rotate concertedly in the course of the ring opening **6**→**9** (see Fig. 4), though it is difficult to classify this process according to the Woodward—Hoffmann rules because of the absence of symmetry elements. It is natural to expect the existence of several rotamers for both forms **7** and **9**. In this work, neither thermodynamic stability nor geometric characteristics of these rotamers were studied, since the studied pathway of enantiomerization does not pass through corresponding points on the PES and they cannot affect the mechanism and the energy barrier to enantiomerization.

Thus, according to our *ab initio* calculations, the enantiotopomerization **6a** ⟷ **6b** of 1,3,2-oxazaborolidene, occurs, as in the case of 1,3,2-oxazaborolidine, by dissociative mechanism with the cleavage

of the B←N bond and the formation of intermediate open structure with an activation barrier of 15.4 kcal mol^{-1}, which is in fairly good agreement with experimental data for boron chelates containing this bond.[2] The fact that internal rotation about the B—O bond makes an appreciable contribution to the reaction coordinate is an essential difference of the mechanism of stereoizomerization of unsaturated derivatives. The magnitude of this contribution is in good agreement with experimental data for chelate boron complexes of the type **4** (R′ = H, CH=NR), in which rotation about the B—O bond is detectable (due to steric effect of the substituent R′) and becomes a stage limiting the overall rate of the process.[13]

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References

1. L. Stryer, *Biochemistry*, W. H. Freeman and Co., San Francisco, 1981.
2. V. I. Minkin, L. E. Nivorozhkin, and M. S. Korobov, *Usp. Khim.*, 1994, **63**, 303 [*Russ. Chem. Rev.*, 1994, **63** (Engl. Transl.)].
3. P. v. R. Schleyer and E.-U. Wurthwein, *Chem. Commun.*, 1982, 542.
4. R. M. Minyaev, G. V. Orlova, and V. I. Minkin, in *III Vsesoyuznaya konferentsiya "Uspekhi khimii azotistykh geterotsiklov"* [*III All-Union Conf. "Adv. in Chemistry of Nitrous Heterocycles"*], Rostov State Univ., Rostov-on-Don, 1983, 192 (in Russian).
5. M.-B. Krogh-Jespersen, J. Chandrasekhar, E. U. Wurthwein, J. B. Kollins, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1980, **102**, 2263.
6. R. Hoffmann, V. I. Minkin, and B. K. Carpenter, *Bull. Soc. Chim. France*, 1996, **133**, 117.
7. J. D. Cox and D. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.
8. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables, J. Phys. Chem. Ref. Data., Suppl.*, 1995, 14.
9. H. Kessler, G. Zimmermann, H. Fietze, and H. Mohrle, *Chem. Ber.*, 1978, **111**, 2406.
10. T. Burgemeister, R. Grobe-Einster, R. Grotstollen, and A. Mannschreck, *Chem. Ber.*, 1981, **114**, 3403.
11. S. Toyota and M. Oki, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1554.
12. A. H. Cowley and J. L. Mils, *J. Am. Chem. Soc.*, 1969, **91**, 2911.
13. M. S. Korobov, G. S. Borodkin, N. I. Borisenko, T. A. Ryskina, L. E. Nivorozhkin, and V. I. Minkin, *J. Mol. Struct. (Theochem.)*, 1989, **200**, 61.
14. J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Pittsburg, Gaussian, Inc., PA, 1996.
15. R. M. Minyaev, *Usp. Khim.*, 1994, **63**, 939 [*Russ. Chem. Rev.*, 1994, **63** (Engl. Transl.)].
16. S. J. Retigg and J. Trotter, *Can. J. Chem.*, 1973, **51**, 1288.
17. A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1986.
18. N. Farfan, D. Castello, P. Joseph-Nathan, and R. Contreras, *J. Chem. Soc. Perkin, 2*, 1992, 527.
19. A. Haaland, *Angew. Chem. Intern. Ed. Engl.*, 1990, **28**, 992.
20. L. R. Thorne, R. D. Suenram, and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.
21. P. M. Kuznesof and R. L. Kuczkowski, *Inorg. Chem.*, 1978, **17**, 2308.
22. J. M. Schulman and R. L. Disch, *J. Mol. Struct. (Theochem.)*, 1995, **238**, 109.
23. R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, and T. F. Koetzle, *Acc. Chem. Res.*, 1996, **29**, 348.
24. M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94, Revision B. 3*, Gaussian, Inc., Pittsburgh (PA), USA, 1995.
25. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347 (*GAMESS, Version 1996*).
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