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Theoretical Design of Planar Molecules with a Nona- and Decacoordinate Central Atom

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Abstract—The maximum coordination number of the central atom in planar molecules generated by now in mole-cular beams was 8. We made use of the chemical bond model developed for planar boron clusters to check the possibility of existence of planar molecules with the coordination numbers 9 and 10. The objects of study were the AlB_9 and AlB_{10}^+ clusters which have local minima corresponding to highly symmetrical D_{9h} and D_{10h} structures, respectively. According to our calculations, the highly symmetrical structure of AlB_9 is a global minimum or a low-lying isomer, and, therefore, it holds promise as a new ligand for coordination chemistry. The energy of the highly symmetrical structure of AlB_{10}^+ with the coordination number 10 is too high, and this structure is hardly synthetically feasible. Thus, 9 is presently the maximum coordination number of an atom in a planar molecule.

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INTRODUCTION

The progress of quantum chemistry over the past two decades has made it possible to predict new molecules. An example is the successful quantum-chemical prediction in 1991 of a series of five-atomic clusters with a tetracoordinate central carbon atom: *cis*-CSi_2Al_2, *trans*-CSi_2Al_2, *cis*-CSi_2Ga_2, *trans*-CSi_2Ga_2, *cis*-CGe_2Al_2, and *trans*-CGe_2Al_2 [1]. These molecules are unusual: They contain planar tetracoordinate carbon, even though a four-bond carbon atom has long, since van't Hoff and Le Bel (1874), been considered to have invariably a tetrahedral environment. In 1970 Hoffmann, Alder, and Wilcox published a fundamental work in which they suggested several approaches to constructing molecules with a planar tetracoordinate carbon atom [2]. However, even these researched expressed certain skepticism as to the possibility of existence of five-atomic molecules with planar tetracoordinate carbon. In particular, they considered it too optimistic to believe that carbon in a simple compound will prefer a planar structure over tetrahedral. Therefore, the theoretical prediction of the above molecules was met with a great deal of skepticism.

In 1999 Lee et al. [3] showed in their combined theoretical and experimental study in 1999 that the structure of the negatively charged ion CAl_4^- is a planar square with the carbon atom in the center [3]. A year later the same researchers discovered that the anions CAl_3Si^- and CAl_3Ge^- and their corresponding neutral molecules CAl_3Si and CAl_3Ge, too, contain a tetracoordinate planar carbon atom [4]. The above five-atomic molecules all are planar, since they have a purely bonding ligand–ligand highest occupied molecular orbital (for details, see [1, 3, 4]). This successful prediction of unusually planar molecules stimulated further theoretical design of other planar molecules with even higher coordinate carbon and other main group atoms [5–21]. In particular, Exner and Schleyer [5] predicted planar molecules with hexacoordinate carbon, and Wang and Schleyer [6] predicted planar molecules with penta- and heptacoordinate carbon [6]. Minkin et al. suggested planar molecules with a heptacoordinate carbon or nitrogen atom, based on quantum-chemical calculations [11]. They also predicted a series of planar octacoordinate carbon, silicon, and phosphorus structures: CB_8, SiB_8, and PB_8^+ [9]. Minyaev et al. [19, 20] showed in their combined theoretical and experimental study that B_8^{2-} and B_9^- are planar structures containing a hepta- and an octacoordinate

central boron atom. The maximum coordination number of the central atom in planar molecules presently generated in molecular beams is eight.

Here we present a quantum-chemical research into the possibility of existence of planar molecules in which the coordination number of the central atom is 9 and 10. As potential candidates we chose the neutral molecule AlB_9 and cation AlB_{10}^+. These systems, according to the chemical bond theory developed for boron clusters [21, 22], are doubly aromatic structures with a ring formed by two-electron two-centered (2*e*–2*c*) B–B bonds (formed by *sp* hybrid orbitals). The first of these systems (AlB_9) has 30 valence electrons, of which 18 are involved in nine 2*e*–2*c* B–B bonds of the outer ring, 6 form a delocalized π bond between the central aluminum atom and the ring, and the rest 6 electrons form a delocalized σ bond of the central aluminum atom with the ring. Analogous analysis for AlB_{10}^+ shows that this cation should have ten 2*e*–2*c* B–B bonds in the outer ring, 6 delocalized π and 6 delocalized σ electrons. The six delocalized π and σ electrons correspond to the Hückel (4*n*+2) rule which makes both molecules doubly aromatic, Therefore, they would be expected to be planar nona- and decahedral structures.

Procedure and Results of Calculations of Molecular Systems with Nona- and Decacoordinate Central Atoms

We started with search for a global energy minimum for the AlB_9 molecule using the Gradient-Embedded Genetic Algorithm (GEGA) software developed at our group by A.N. Alexandrova [23, 24]. The energies, gradients, and force constants were calculated using B3LYP–DFT with the small 3-21G basis set. The five lowest energy isomers found by GEGA were reoptimized with the subsequent calculation of vibration frequencies by means of B3LYP/6-311+G*. The full energies of these isomers were recalculated using CCSD(T)/6-311+G(2df) with the B3LYP/6-311+G* geometries.

With AlB_{10}^+, we restricted ourselves to two isomers. The geometric parameters and vibration frequencies of these isomers were calculated by the B3LYP/6-311+G* method, and their full energies were recalculated by the CCSD(T)/6-311+G(2df) method with the B3LYP/6-311+G* geometry. The calculations were performed using the Gaussian03 program [25]. The structures and molecular orbitals were drawn using the MOLDEN3.4 program [26].

The five lowest energy isomers of AlB_9, found by GIGA, are depicted in Fig. 1a. Isomer **II** with a nona-coordinate aluminum atom in the center corresponds to a global minimum on the PES calculated by means of B3LYP/6-311+G*.

Isomer **I** which can be considered as a structure obtained by substitution of one peripheral boron atom by aluminum in the global minimum structure of the B_{10} cluster [21, 22] is 6.1 kcal mol^{-1} higher in energy than jвыше по энергии, чем isomer **II** obtained by B3LYP/6-311+G* calculations However, according to CCSD(T)/6-311+G(2df) calculations with the B3LYP/6-311+G* geometry, isomer **I** is a global minimum structure. Isomer **II** at the latter level of theory is as little as 1.0 kcal mol^{-1} higher in energy than isomer **I**. Therefore, these results allow us to draw no conclusions as to what of the isomers corresponds to a global minimum, and we are inclined to consider them energetically degenerate.

Isomers **III** and **V,** are also derivatives of the global minimum structure of the B_{10} cluster, with peripheral boron atoms substituted in two other possible positions. These isomers are both higher in energy than isomers **I** and **II**. Geometry optimization of the structure in which one of the two central boron atoms in the B_{10} cluster is substituted by aluminum leads to structure **IV** with an ionic bond between Al^+ and B_9^-.

For the cluster AlB_{10}^+ we only compared the two structures depicted in Fig. 1b. Isomer **VII** with a decacoordinate planar aluminum center is much higher in energy than isomer **VI** which can be considered as a complex of Al^+ with the B_{10}.cluster. Even though the global minimu structure of the AlB_{10}^+ cluster is unknown, the fact that isomer **VII** is much higher in energy than isomer **VI** allows us to rule out isomer **VII** from possible candidate decacoordinate planar structures.

Thus, as follows from our calculations, nine is a maximum coordination number of the central atom in a planar molecule where it surrounded by a ring of boron atoms. Structure **VII** for the AlB_{10}^+ cluster, while being a local minimum, has a too high energy for this structure to be realized in practice in any chemical compound. The energy gap is also too low for isomer **VII** to form in any appreciable amounts in experiments with molecular beams or under matrix isolation conditions.

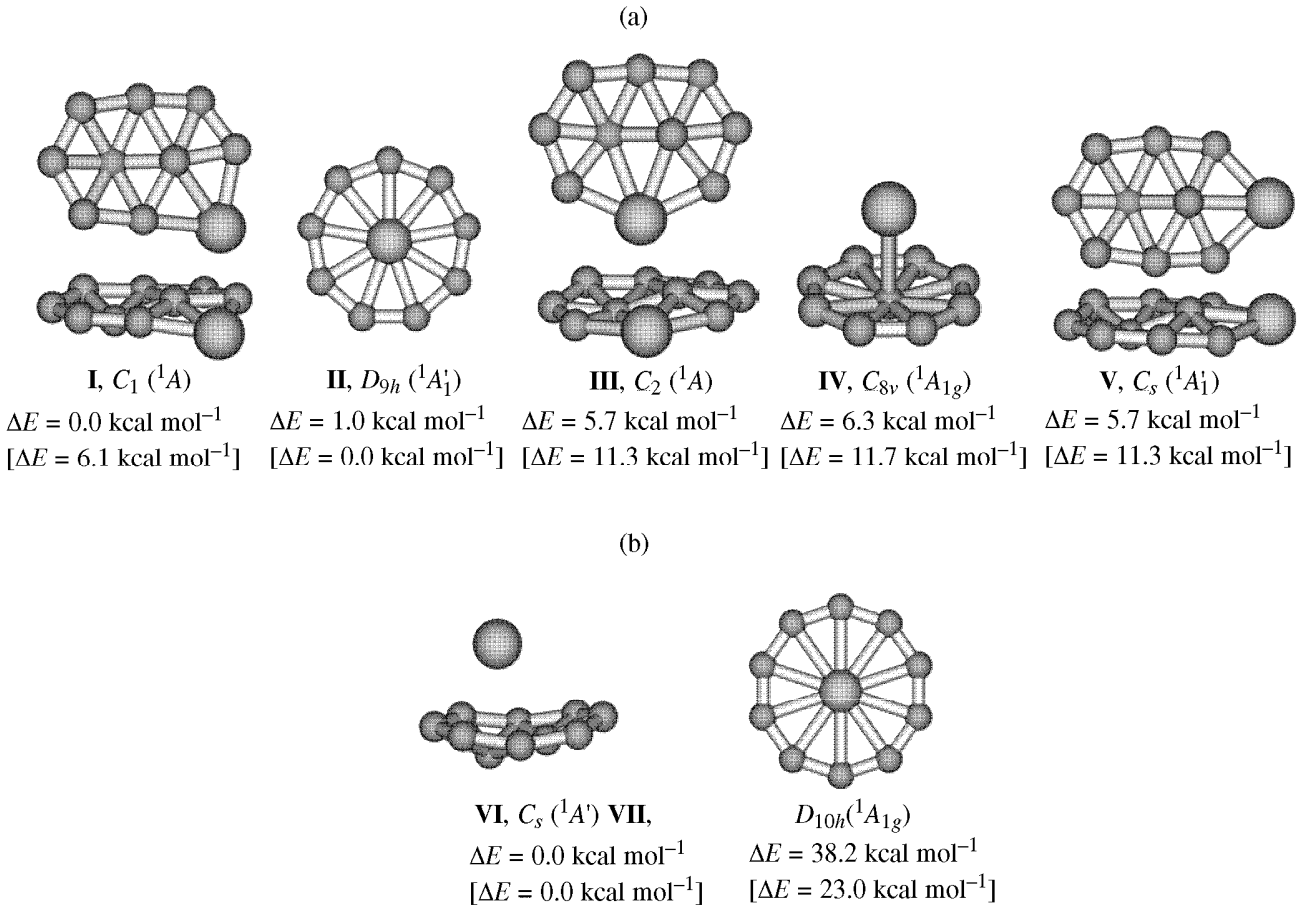

Fig. 1. Molecular systems (a) AlB_9 and (b) AlB_{10}^+ with a nona- and decacoordinate central atom.

Our choice of the AlB_9 and AlB_{10}^+ clusters as possible candidate molecules with a nona- or decacoordinate atom in a planar structure is motivated by unique features of chemical bonds in boron clusters. Even though the crystal lattice of boron is formed by three-dimensional fragments (icosahedrons),isolated boron clusters, at least those containing up to 15 atoms, are either planar or quasiplanar [21, 22]. The planar or quasiplanar structure of boron clusters is explained by the fact that they have an outer ring of 2*e*–2*c* B–B bonds. Additional bonding in boron is provided by delocalized σ and π bonds. Clusters in which the number of delocalized σ and π electrons is 4*n*+2 are double aromatic and, therefore, highly symmetrical, which makes them suitable candidate planar molecules with a high-coordinate central atom.

Aluminum was chosen for the central atom, since it is less electronegative than boron. This is important, because the central atom is only involved in delocalized bonds with peripheral atoms, whereas ring atoms are additionally involved in the formation of ring 2*e*–2*c* bond; as a result, electronegative atoms will prefer to reside in the ring rather than in the molecular center.

Molecular orbital analysis of AlB_9 and AlB_{10}^+ (Figs. 2a and 2b) points to the same nature of bonding as in purely boron clusters.

The HOMO-4 through HOMO-8 in AlB_9 can be localized by the NBO method on two-center B–B bonds with effective filling numbers of 1.95 e, which is quite close to the classical number 2 for a 2*e*–2*c*

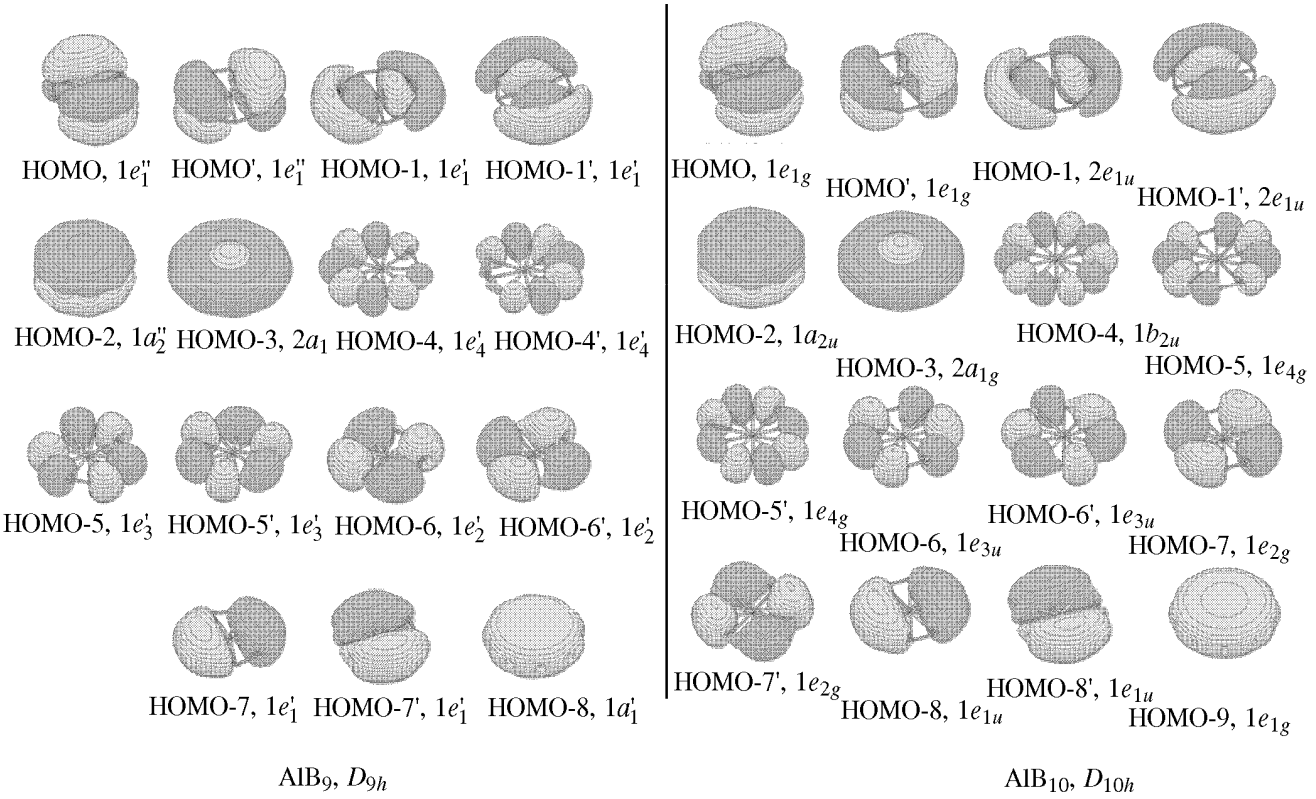

Fig. 2. Molecular orbitals of the AlB_9 and AlB_{10}^+ clusters.

bond. The NBO analysis showed that the peripheral boron atoms in these bonds are *sp*-hybridized. The HOMO through HOMO-3 are impossible to localize, which means that they responsible for the delocalized bond between the central aluminum atom and the peripheral ring. The HIOMO and HOMO-2 are π orbitals (they are similar in structure to benzene π orbitals), i.e. they provide π-aromaticity of the molecule. The HOMO-1 and HOMO-3 are σ orbitals, and they provide σ-aromaticity of the cluster.

The HOMO-4 through HOMO-9 in AlB_{10}^+ can be localized by the NBO method on two-center B–B bonds with effective filling numbers of 1.96 e. The NBO analysis showed that the peripheral boron atoms in these bonds are *sp*-hybridized. The HOMO through HOMO-3 cannot be localized; that is to say, they responsible for the delocalized bond between the central aluminum atom and the peripheral ring. The HOMO and HOMO-2 in AlB_{10}^+ are π orbitals, i.e. they make the molecule π-aromatic. The HOMO-1 and HOMO-3 are σ orbitals responsible for σ-aromaticity of the cluster.

The above-described chemical bonding in the AlB_9 and AlB_{10}^+ clusters explains the planat structure and high simmetry of isomers **II** and **VII**. Isomer **VII** of AlB_{10}^+ is much less stable than isomer **VI**, since the radius of the outer boron ring is too large for a single central atom to maintain 12 delocalized electrons. Substitution of aluminum by gallium or indium in the ring center fails to make the decacoordinate structure much more stable, despite the larger atomic radius of gallium or indium.

CONCLUSION

The chemical bond model developed for planar boron clusters was used to check the possibility of existence of planar molecules with the coordination numbers 9 and 10. The objects for study were the AlB_9 and AlB_{10}^+ clusters which have local energy minima corresponding to highly symmetrical D_{9h} and D_{10h} structures. The highly symmetrical structure of the AlB_9 molecule is a global minimum or a low-lying isomer, and, therefore, it holds promise a new ligand for coordination chemistry. The highly symmetrical structure of AlB_{10}^+ with the coordination number 10 has

a too high energy and is hardly interesting for synthetic chemistry. Thus, at present 9 is the maximum coordination number of an atom in a planar molecule.

REFERENCES

1. Schleyer, P.v.R. and Boldyrev, A.I., *J. Chem. Soc., Chem. Commun.*, 1991, p. 1536.
2. Hoffmann, R, Alder, R.W., and Wilcox, C.F.Jr., *J. Am. Chem. Soc*., 1970, vol. 92, p. 4992.
3. Li X., Wang L.S., Boldyrev A.I., Simons J., *Ibid*., 1999, vol.. 121, p. 6033.
4. Wang L.S., Boldyrev A.I., Li X., Simons J., *Ibid*., 2000, vol. 122, p. 7681.
5. Exner, K. and Schleyer, P.v.R., Science, 2000, vol. 290, p. 1937.
6. Wang, Z.-X. and Schleyer, P.v.R., *Ibid*., 2001, vol. 292, p. 2465.
7. Erhardt, S., Frenking, G., Chen, Z., and Schleyer, P.v.R., *Angew. Chem. Int. Ed.*, 2005, vol. 44, p. 1078.
8. Ito, K., Chen, Z., Corminboeuf, C., Wannere, C.S., Zhang, X.H., Li, Q.S., and Schleyer, P.v.R., *J. Am. Chem. Soc*., 2007, vol. 129, p. 1510.
9. Minyaev, R.M., Gribanova, T.N., Starikov, A.G., and Minkin, V.I., *Mendeleev Comm*., 2001, vol. 11, p. 213.
10. Gribanova, T.N., Minyaev, R.M., and Minkin, V.I., *Zh. Neorg. Khim*., 2001, vol. 46, p. 1340.
11. Minyaev, R.M., Gribanova, T.N., Starikov, A.G., and Minkin, V.I., *Dokl. Ross. Akad. Nauk, Ser. Khim*., 2002, vol. 382, p. 785.
12. Minkin, V.I. and Minyaev, R.M., *Mendeleev Comm*., 2004, vol. 14, p. 43.
13. Havenith, R.W.A., Fowler, P.W., and Steiner, E., *Chem. Eur. J*., 2002, vol. 8, p. 1068.
14. Li, S.-D., Miao, C.-Q., Guo, J.-C., and Ren, G.-M., *J. Am. Chem. Soc*., 2004, vol. 126, p. 16227.
15. Li, S.-D., Miao, C.-Q., and Ren, G.-M., *Eur. J. Inorg. Chem*., 2004, p. 2232.
16. Li, S.-D., Guo, J.-C., Miao, C.-Q., and Ren, G.-M., *J. Phys. Chem. A*, 2005, vol. 109, p. 4133.
17. Li, S.-D. and Miao, C.-Q., *Ibid*., 2005, vol. 109, p. 7594.
18. Li, S.-D., Miao, C.-Q., Ren, G.-M., and Guo, J.-C., *Eur. J. Inorg. Chem*., 2006, p. 2567.
19. Zhai, H.-J., Alexandrova, A.N., Birch, K.A., Boldyrev, A.I., and Wang, L.S., *Angew. Chem. Int. Ed*., 2003, vol. 42, p. 6004.
20. Alexandrova, A.N., Zhai, H.-J., Wang, L.S., and Boldyrev, A.I., *Inorg. Chem*., 2004, vol. 43, p. 3552.
21. Alexandrova, A.N., Boldyrev, A.I., Zhai, H.-J., and Wang, L.S., *Coord. Chem. Rev*., 2006, vol. 250, p. 2811.
22. Zubarev, D.Yu. and Boldyrev, A.I., *J. Comput. Chem.*, 2007, vol. 28, p. 251.
23. Alexandrova, A.N., Boldyrev, A.I., Fu, Y-J., Wang, X.-B., and Wang, L.S., *J. Chem. Phys*., 2004, vol. 121, p. 5709.
24. Alexandrova, A.N. and Boldyrev, A.I., *J. Chem. Theory Comput*., 2005, vol. 1, p. 566.
25. Frisch, M.J., et al. *GAUSSIAN 03*, Rev. C. 02, Pittsburgh, PA: Gaussian, 2003.
26. Schaftenaar, G., MOLDEN3.4, the Netherlands: CAOS/CAMM Center, 1998.