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B_{18}^{2-}: A Quasi-Planar Bowl Member of the Wankel Motor Family

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A quasi-planar member of the so-called 'Wankel motor' family, B_{18}^{2-}, is found. This boron cluster is an electronically stable dianion and a concentric doubly σ- and π-aromatic system. The inner B_6 unit in B_{18}^{2-} undergoes quasi-free rotation inside the perimeter of B_{12} ring. The absence of any localized σ-bond between the inner ring and the peripheral boron atoms makes the system fluxional.

Recently, the groups of Boldyrev and Wang reported the detection of a beautiful boron wheel formed by nineteen boron atoms (B_{19}^-).[1] This cluster contains a pentagonal six-boron fragment enclosed by the other thirteen boron atoms. More recently, we found that the pentagonal-hub and the outer boron ring can rotate almost freely in opposite directions, similar to a Wankel motor.[2] This type of dynamical behavior is similar to that found in some aromatic boron wheels (C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^+$) with more than one carbon at the center.[3] Unfortunately, in all those borocarbon wheels, isomers having carbon atoms at the outside ring are lower in energy. In 2011, we found that B_{13}^+ also exhibits a similar dynamical behavior like that of B_{19}^- with an almost free rotation of the inner B_3 moiety surrounded by the B_{10} ring.[4] The group of Alexandrova further suggested a very interesting idea to control the direction of rotation of the B_3 triangle in B_{13}^+ by applying an external circularly-polarized infrared laser.[5] Tai et al. also showed that $B_{20}^{-/2-}$ with a hexagonal subunit surrounded by the B_{13} ring exhibits the same kind of fluxionality.[6]

In this communication, the fifth member of this family is presented. Our computations show that the most stable structure of B_{18}^{2-} comprises a pentagonal six-boron fragment, surrounded by the B_{12} ring, but in contrast to the B_{19}^- system, it has a bowl-shape and thus deviates from the planarity of the other family members. Nevertheless, molecular dynamics simulations indicate that the system behaves as a 'Wankel motor'. The chemical bonding analysis and the aromaticity study are performed in detail to provide further insight into the fluxionality and the stability of the system. The interaction of the B_{18}^{2-} with a lithium cation is also examined.

The potential energy surfaces (considering both singlet and triplet states) of B_{18}^{2-} and $B_{18}Li^-$ are systematically explored using the gradient embedded genetic algorithm (GEGA) as is implemented in the Kaxan program.[7] The PBE0 functional in conjunction with the D95 basis set is used for the energy, gradient, and force computations using the Gamess suite of programs.[8] The geometries obtained from the GEGA computations[9] are further reoptimized at the TPSS/def2-TZVP level.[10] Harmonic vibrational frequencies are also analyzed at the same level to characterize the nature of all stationary points and to compute the zero point energy (ZPE) corrections. The Adaptive Natural Density Partitioning (AdNDP) method[11] is performed at the TPSS/def2-TZVP level. Born-Oppenheimer Molecular-Dynamics (BO-MD) simulations are carried out at the

TPSS/DZVP level in deMon2K,[12] starting from the global minimum geometry of the B_{18}^{2-} system.

We have found that the global minimum structure of B_{18}^{2-} is not planar, it is rather a bowl-like structure having C_s symmetry and is composed of an outer B_{12} ring connected to a slightly out-of-plane inner B_5 ring, which is further capped by one B atom (see Fig. 1). The centers of the B_{12} ring and B_5 ring are separated by ~ 0.6 Å whereas the central B atom resides ~ 0.5 Å above the B_5 ring. Therefore, the depth of the bowl is around 1.1 Å. The global minimum is only 1.9 kcal/mol more stable than the second low-lying planar D_{3h} isomer (see Fig. 1-SI). Therefore, in an experimental situation, at a given temperature both the isomers may exist in different proportions in the final products. Note that similar central capped pentagonal boron moiety is found in recently reported B_{24}^- cluster.[13] The groups of Wang and Boldyrev[14] detected the B_{18}^- cluster in the gas phase via photoelectron spectroscopy (PES) and also found its global minimum in silico. They found that the lowest energy isomer of B_{18}^- corresponds to C_{3v} symmetry, in which the central B_3 unit resides around 0.5 Å away from the molecular plane making it a quasi-planar molecule. Note that the C_{3v} geometry of the B_{18}^- cluster is similar to the second lowest energy form of B_{18}^{2-}. The out-of-plane central B_3 unit in the C_{3v} isomer of B_{18}^- comes to the plane in the D_{3h} isomer of the B_{18}^{2-} cluster. The extra negative charge in the system may help in expanding the peripheral boron ring a little bit, which indeed makes sufficient space in fitting the B_3 unit within the molecular plane. Furthermore, the second lowest energy isomer of B_{18}^- is similar to the global minimum of B_{18}^{2-}. The C_s isomer in B_{18}^- is only 1.6 kcal/mol higher in energy than its C_{3v} form. In fact, they identify both isomers in the photoelectron spectrum. In our case, the energy difference between the first two lowest-lying isomers is 2.5 kcal/mol computed at the CCSD(T)/def2-TZVP//TPSS/def2-TZVP level of theory (Fig 1-SI).
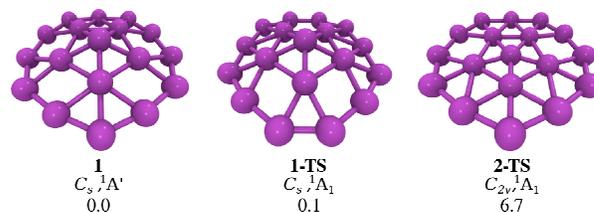

1
$C_s, {}^1A'$
0.0

1-TS
$C_s, {}^1A_1$
0.1

2-TS
$C_{2v}, {}^1A_1$
6.7

Fig. 1 Global minimum of B_{18}^{2-} (**1**) and the transition states related to the rotation (**1-TS**) and inversion (**2-TS**). The relative energies are in kcal·mol⁻¹ units.

The interesting characteristic of the C_s isomer of B_{18}^{2-} cluster is that the mode of its smallest vibrational frequency (102.2 cm⁻¹) corresponds to a rotation of inner B_6 unit, which is an important indicator to act as a 'Wankel motor'. Following the frequency of this mode, a structure corresponding to a transition state (TS) with an imaginary frequency of 111.1 i cm⁻¹ is found. The mode of this

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imaginary frequency is also related to the rotation of the inner B_6 unit. The energy difference between **1** and **1-TS** is almost negligible (0.1 kcal/mol) (see Fig. 1). Therefore, such a negligible rotation barrier hints at an almost free rotation of the B_6 unit within the B_{12} ring. This is exactly what we have found in the BO-MD simulation. The inner B_6 unit rotates almost freely inside the perimeter of the B_{12} ring during the simulation. The movie showing this fluxionality during the BO-MD simulation carried out at 900 K is provided in electronic supporting information (ESI). The rotation of B_6 unit is found to be accompanied by the simultaneous bond breaking and bond making between the B_6 unit and peripheral B_{12} ring. Note that it is the first quasi-planar system, which shows such fluxionality. We have also located the transition state for the bowl-to-bowl inversion of the C_s isomer (structure 2-TS in Fig. 1). The inversion barrier is found to be 6.7 kcal/mol. This barrier is lower than that found in sumanane (19.6 kcal/mol) or coranulene (10.2 kcal/mol), the classical bowl-like carbon structures.[15]
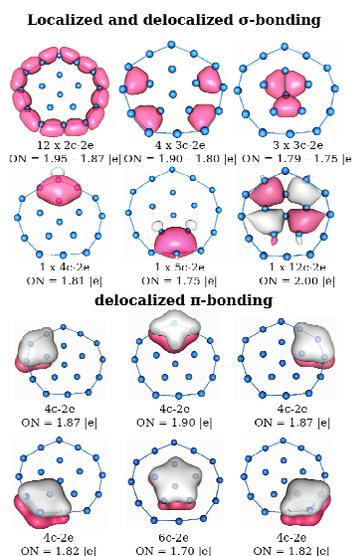

Localized and delocalized σ-bonding

delocalized π-bonding

Fig. 2 Adaptive Natural Density Partitioning (AdNDP) Analysis of **1** at the TPSS/def2-TZVP level.

In B_{19}^- and B_{13}^+, the absence of localized 2c-2e σ-bonding between the inner rotating unit and outer ring favors such free rotation. Now, let us analyze the chemical bonding situation in our present case by employing the AdNDP method. The occupation number (ON) represents the number of electrons involved in a bond. The ONs recovered for all the bonds in the B_{18}^{2-} system are quite close to the limiting value of 2.0 |e| per bond. This analysis shows that there are 12 two-center two-electron (2c-2e) localized σ-bonds in the peripheral B_{12} ring, however, the rest of the bonding is of the delocalized type (see Fig. 2). There are 10 delocalized σ-bonds, out of which seven are delocalized over three B atoms (7 x 3c-2e), one is over four B atoms (4c-2e), one is over five B atoms (5c-2e) and the last one is delocalized over 12 B atoms (12c-2e). Among them, three 3c-2e σ-bonds are involved within the inner B_6 unit, whereas the remaining delocalized σ-bonds are responsible for the bonding between the B_6 unit and the outer B_{12} ring. The AdNDP analyses also show that there are six delocalized π-bonds: five being delocalized over four B atoms (5 x 4c-2e) and one over six inner

B atoms (6c-2e). The electron density of each of the five 4c-2e π-bonds remains engaged over the three peripheral B atoms and one B atom of the inner B_5 ring. Therefore, from the AdNDP analysis, we can see that there is no localized bond between the outer B_{12} ring and inner B_6 unit; they are only linked via delocalized multicenter-2e σ- and π-bonds. Such delocalized bonds easily migrate from one position to the other during rotation of the B_6 unit; hence such arrangements allow the molecule to show the fluxional behavior.

The total number of delocalized σ- and π-electrons in B_{18}^{2-} is 20 and 12, respectively. Using the Hückel rule of aromaticity as such, the overall system should be both σ- and π-antiaromatic. But separating two distinct regions (the inner and outer ring), the conclusion is different. Three 3c-2e σ-bonds and one 6c-2e π-bond are involved within the B_6 unit satisfying the Hückel rule (for σ-bonds, 4n + 2 = 6; n = 1 and for π-bond, 4n + 2 = 2; n = 0). The inner B_6 moiety is, therefore, both σ- and π-aromatic. Now, the region in between the B_6 unit and the peripheral B_{12} ring contains 14 delocalized σ-electrons (4n + 2 = 14; n = 3) and 10 delocalized π-electrons (4n + 2 = 10; n = 2) once again satisfying the (4n + 2) rule (see Fig. 2). It should be noted that the electron density of the 12c-2e σ-bond remains within both regions, but since the maximum electron density is located over the area in between the B_6 unit and the peripheral ring, we have counted it for this region only. Therefore, the B_{18}^{2-} system may be considered to be both concentric doubly σ- and π-aromatic system satisfying individually the Hückel rule. Here it will be worthy to acknowledge the contributions from Schleyer and co-workers in introducing the concept of double aromaticity.[16] Further, the C_{3v} isomer of the B_{18}^- system was categorized as an all-boron analogue of coronene, however, the C_s isomer is one e^- less to be the all-boron analogue of coronene.[14] Now, here the C_s isomer of the B_{18}^{2-} system has a closed-shell configuration having doubly occupied π-type HOMO (see Fig. 2-SI). Therefore, it may also be considered to be an all-boron analogue of coronene.
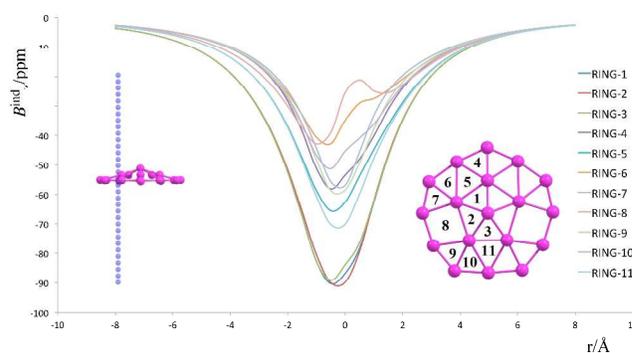

Fig. 3 B^{ind}_z profiles of B_{18}^{2-} computed at the PW91/def2-TZVP level. The profile starts at the geometrical center of each three and four membered ring.

Quite recently, Nguyen and co-workers[6,17] suggested the model of particle in a circular box to understand the orbital distribution in the boron wheels. A system will show the disk-aromaticity if its π-electrons fully occupy the lowest eigenstates of the model in the ascending order of 1σ, 1π, 1δ, 2σ, 1Φ, 2π and so on. Therefore, the systems with 2, 6, 10, 12, 16, 20…. π-electrons lead to a completely occupied configuration, hence show the disk-aromaticity. In our case, the B_{18}^{2-} system has 12 π-electrons with $(1σ)^2(1π)^4(1δ)^4(2σ)^2$ configuration, therefore, it is a disk-aromatic

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system. The shapes of the π-MOs of the B_{18}^{2-} system and the lowest wave functions for particle in a circular box are shown in Fig. 3-SI.

Further, to prove the doubly σ- and π-aromaticity in B_{18}^{2-}, analysis of the z-component of induced magnetic field $(B^{ind}_z)^{18}$ is done. Positive and negative values of B^{ind}_z indicate the paratropic (antiaromaticity) and diatropic (aromaticity) behavior of the system, respectively. The B^{ind}_z profiles computed at the centers of the three and four membered rings located either within the inner B_6 unit or in between the B_6 and outer B_{12} ring are displayed in Figure 3. Clearly, the magnetic response is highly diatropic in nature within the plane of the small rings and although gradually diminishes with the distance from the center of the ring, it still maintains a high value (in absolute sense). Even at 4 Å above or below the plane, the B^{ind}_z value is found to be equal or larger (in absolute sense) than -10 ppm. The inner rings (1, 2 and 3) show more diatropic character (both in plane and out of plane) than the outer rings showing their larger aromaticity (both σ and π) than the same. The four membered ring (8) shows the smallest diatropic response. Therefore, negative values of B^{ind}_z at the plane and perpendicular to the plane of the rings in the both regions confirm the concentric doubly σ- as well as doubly π-aromatic nature of the B_{18}^{2-} system.

Finally, we computed both vertical and adiabatic electron dissociation energy (VEDE and AEDE) at different density functional based methods, outer-valence Green's function (OVGF) method and wave function based method (see Table 1-SI).[19,20] Except the VEDE values calculated by using so-called crude direct approach, Koopmans' theorem (KT) at the TPSS level, the other results with more reliable approach than KT show the bound nature of HOMO electron in B_{18}^{2-}. Therefore, it is a stable dianion with respect to spontaneous electron detachment. Nevertheless, we have also examined the possible to stabilize the dianion adding Li+ as counterion. In the global minimum of $B_{18}Li^-$, the structure of the boron skeleton is identical to that of B_{18}^{2-} and the Li^+ cation is found to bind with one B center of the concave surface of the inner B_5 ring having a B-Li distance of 2.217 Å (see Fig. 4-SI).

In conclusion, B_{18}^{2-} is the fifth member of the 'Wankel motor' family. The inner B_6 unit rotates within the peripheral B_{12} ring with an almost negligible rotation barrier. The chemical bonding analyses show that the inner B_6 moiety and the outer ring are connected through only multicenter-2e bonding. The absence of any localized bond therein facilitates such fluxionality. The B_{18}^{2-} cluster may be viewed as a concentric doubly σ- as well as doubly π-aromatic system. The analysis of induced magnetic field further confirms this doubly aromaticity. The aromaticity in the B_{18}^{2-} cluster can also be justified by using the concept of disk-aromaticity. The computations of VEDE and AEDE at several levels reveal that it is a stable dianion system with bound HOMO electron. Further, the B_{18}^{2-} cluster in presence of a counter-ion (Li^+), that is the LiB_{18}^- system, is also viable with high VEDE.

Notes and references

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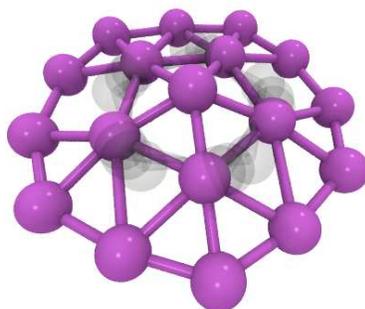*^{c} Center of Functional Nanomaterials (NanoFun), School of Engineering and Science, Jacobs University Bremen, Bremen, 28759, Germany.*
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