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The B_{19}^- anion and other boron species have been dubbed 'Wankel motors' for the almost barrierless rotation of inner and outer concentric rings relative to each other in these compounds. A single substitution in B_{19}^- is shown to shut down the well-established fluxionality in the anion. A carbon atom substituted in the structure to give a neutral CB_{18} species is shown computationally to enforce bond localization.

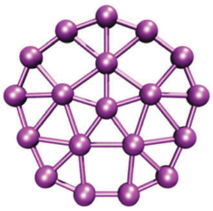

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Fig. 1 Global minimum structure of B_{19}^-.

The monoanionic nineteen boron atom cluster (B_{19}^-) adopts a beautiful ring structure with a central atom surrounded by a pentagonal core that is itself surrounded by a thirteen boron atom outer ring (Fig. 1). Both the central six-atom pentagon and the outer thirteen-atom ring independently satisfy the $(4n + 2)\pi$ Hückel rule (with two and ten electrons, respectively). Huang *et al.* established the structure and chemical bonding by a joint photoelectronic spectroscopy and theoretical study.[1] More recently, we reported the remarkable fluxional behaviour of the B_{19}^- cluster; it shows an almost free internal rotation of the pentagonal-shaped hub within the co-planar B_{13} ring, which is evident from the Born Oppenheimer Molecular Dynamics (BO-MD) simulations indicating motions similar to those of a Wankel motor.[2]

This kind of fluxional behaviour is not exclusive to B_{19}^-. Quite recently, B_{13}^+, B_{18}^{2-}, and B_{20}^- have been added to the select list of Wankel boron clusters that are expected to exhibit fluxional behaviour at relatively low temperatures.[3] One question that immediately arises, however, is: how can one control, initiate, or direct the rotation of such systems? Zhang *et al.* proposed to trigger the rotation of the outer ring in B_{13}^+ in a given direction by applying an external laser field.[4] Without an external field, the barrier that B_{13}^+ must overcome in order to rotate is only 0.25 kcal mol^{-1} and, given the symmetry of the system, the rotation may occur in both directions with the same probability. However, if an electric field is applied in the plane of the molecule, perpendicular to the molecular axis, the symmetry of the system is broken such that the ring prefers to rotate unidirectionally.[5]

This communication addresses the nature of the fluxional behaviour of the neutral CB_{18} cluster, which is the product of a substitution of one boron atom by carbon in B_{19}^-. We found that although the B_{19}^- and CB_{18} rings are isoelectronic and structurally similar, the neutral borocarbon system does not exhibit the same fluxional behaviour as the pure boron anion.

It is important to mention at this point that in the gas-phase, several clusters are produced under thermally excited conditions and the mixture of products is governed by thermodynamics.[6] In most cases, however, only one isomer – the global minimum – remains. This is the case for B_{19}^-, where Wang and Boldyrev found a perfect match between the photoelectron spectrum of this cluster and that theoretically obtained for structure **1**.[1] In our case, however, it is not clear that to start with a substitution at any single boron site in the B_{19}^- atom by carbon will produce a stable CB_{18} cluster that will maintain the same basic structure and fluxionality. In this work we examine computationally the influence on the fluxionality of the system

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of a single point substitution of a C atom for a B^- one to generate a neutral analogue of structure **1**. Assuming that the same general minimum energy geometry of B_{19}^- would be preferred by CB_{18}, there are at least three positions where the lone carbon atom could be located – at the centre of the cluster, in the inner pentagon, or in the outer ring.

In order to do a systematic lowest-energy isomer search on all of the candidates, we decided to employ a stochastic search. Our computational procedure involves the gradient embedded genetic algorithm (GEGA)[7] and a kick procedure[8] to generate starting structures, establishing a hierarchical screening at the density-functional theory (DFT) and high level *ab initio* methods to identify the most stable isomer. The discussion is based on results obtained at the PBE0/def2-TZVP[9] level. All these computations were done using the Gaussian 09 suite of programs.[10] Born–Oppenheimer molecular-dynamics (BO-MD) simulations and the computation of the electronic properties, including the induced magnetic field, have been carried out at the PBE/DZVP level using the deMon2K software package.[11]

The five most stable local minima of CB_{18} (**2**), which were found within 20 kcal mol^{-1} above the global minimum, are shown in Fig. 2. In the global minimum (**2-A**), the carbon atom is located at the outer ring fragment, *i.e.*, the carbon atom shows a substantial preference for a spot on the outer ring over the inner pentagonal unit or the centre of the boron wheel avoiding extreme hypercoordination as described by Boldyrev and Wang.[12] Indeed, the carbon atom in the other four lowest energy species remains in the outer ring. The energy difference between the lowest-energy isomer and the next most stable isomeric form is only 3.1 kcal mol^{-1}. When carbon is placed at the internal pentagon or even at the centre of the ring, the relative energy is 40 kcal mol^{-1} higher than **2-A** (Fig. S1, ESI†).

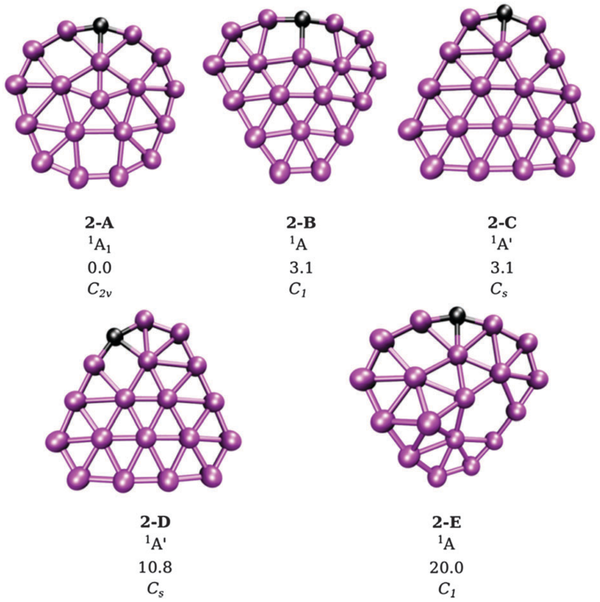

Fig. 2 Optimized isomers of CB_{18}, only isomers under 20 kcal mol^{-1} are shown. The relative energies are in kcal mol^{-1} units. All structures were optimized at the PBE0/def2-TZVP level.

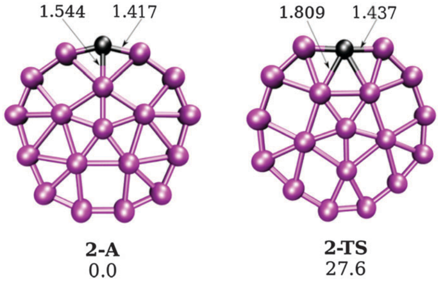

Fig. 3 Global minimum structure of CB_{18} (A) and the transition state related to the inner pentagon-shaped hub (B). The relative energies are in kcal mol.

The most relevant geometrical parameters of **2-A** are summarized in Fig. 3. The C–B distance connecting both rings is longer (1.544 Å) than that computed for the external ring. At first glance, carbon does not drastically alter the structure of B_{19}^-. The vibrational analysis shows that **2-A** is a minimum and the smallest vibrational frequency corresponds to a soft mode of 56 cm^{-1}, assigned to the out-of-the-plane movement of the inner pentagon. This is different from B_{19}^- (structure **1**), where the lowest frequency is related to the rotation of the pentagon fragment. In the case of B_{19}^-, the barrier to the rotation of the pentagon-shaped hub and the B_{13} wheel in the opposite direction is negligible (less than 0.1 kcal mol^{-1}).

However, substituting for a carbon atom in the outer ring modifies this barrier drastically. For CB_{18}, the transition structure (**2-TS**) for this rotation is 27.6 kcal mol^{-1} higher in energy than the global minimum, preventing the rotation of the inner and outer rings relative to each other at low temperatures (see Fig. 3). So, despite the structural similarities between B_{19}^- and CB_{18}, it appears to be unlikely that the latter will demonstrate any fluxional character similar to the former, especially at relatively low temperatures. BO-MD simulations at the PBE/DZVP level support our observations on the dynamical behaviour of B_{19}^- and the absence of fluxionality in CB_{18}. The simulations were started from the equilibrium geometries, with random velocities assigned to the atoms, and both systems were equilibrated for 300, 600, and 900 K, using a Nosé–Hoover thermal bath for 20 ps after which a set of 50 ps trajectories were computed. In both cases, for B_{19}^- and CB_{18}, during the BO-MD simulations the planar structure is essentially maintained, but no internal or external ring rotation is observed in CB_{18} even for 900 K (see movies S1 and S2, which have been submitted as part of the ESI†).

Why would a system that is isoelectronic and essentially isostructural to B_{19}^- exhibit a totally different dynamical behaviour? The answer we found is in a few but significant differences in the chemical bonding in the C substituted system. According to the Adaptive Natural Density Partitioning (AdNDP) analysis,[13] in CB_{18} there are twelve valence π-electrons with two of them participating in the bonding of the central six boron atoms and the other ten being responsible for the bonding between the $B_{12}C$ external ring and the internal B_6 pentagon (Fig. 4). This π-electron distribution is analogous to that found in B_{19}^-.[1] The extra forty-six electrons participate in the σ-bonding. However, the σ-electron distribution is considerably different in CB_{18} compared to B_{19}^-.

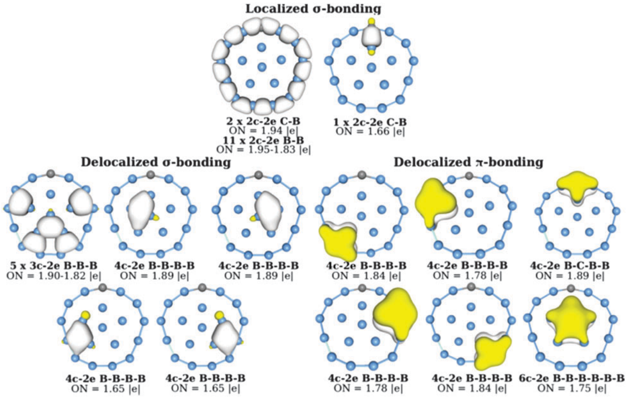

Fig. 4 Adaptive natural density partitioning (AdNDP) analysis of **2-A** at the PBE0/def2-TZVP level.

Twenty-six σ-electrons are involved in localized bonding and they form eleven peripheral 2c–2e B–B bonds and two 2c–2e C–B bonds. The difference lies in the presence of one extra localized 2c–2e C–B bond, which connects the peripheral and the internal pentagon rings. This is the primary reason for the radically different dynamical behaviour in the CB_{18} clusters (Fig. 4) compared to the nineteen-boron anion.

The quest for molecular machines is ongoing. The recent identification of concentric boron ring systems in which one ring rotates relative to the other[2,3] provides an additional device with potential utility in such machines. It is necessary, however, to develop a systematic understanding of how to control, and direct the motion of these 'boron Wankel motors'. This achievement would enable us to identify the key electronic and geometry characteristics of boron clusters that are necessary for the observed fluxionality and strategies (with similar effects) to promote functionality in other homonuclear or heteronuclear clusters.

Constraining the almost barrierless fluxionality in the boron clusters may be desirable under certain conditions as well. We found in this work that a single point substitution of a B anion by an isoelectronic C atom increases the barrier to rotation by over 27 kcal mol^{-1}. This escalation in the rotational barrier arises from 'a spoke in the wheel'. The C atom in the CB_{18} cluster shows a definite preference for bonding in the outer ring rather than at any of the alternative sites held by the six inner boron atoms. This C center forms, however, a localized and relatively stable 2-center 2-electron bond to a single B atom in the inner pentagonal ring (see Fig. 4). The initially free rotation of the inner and outer rings relative to each other is, therefore, rendered impossible at low temperatures. The other σ- and π-bonding interactions in the cluster, which we have identified quite clearly in this work using AdNDP, are nearly identical in both the fluxional B_{19}^{-} and the far more rigid CB_{18} systems. The latter C substituted analogue, which adopts the same basic geometry and has the same electron count as B_{19}^{-}, promotes charge localization in single C–B bonds such that the anticipated fluxional activity disappears completely.

In summary, our results provide some significant initial pieces of evidence that fluxionality in boron clusters can be readily quenched by a simple substitution for C at one site in the cluster in this case.

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