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Molecular Motors

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And Yet It Rotates: The Starter for a Molecular Wankel Motor

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molecular motors

The transfer of everyday objects, even complex ones such as machines, to the molecular level marks the ultimate limit of miniaturization. Many such analogies are known in chemistry, for example molecular containers, molecular sieves, and molecular switches. "Molecular motors" appears to be a very attractive term that has been taken up by biophysicists, referring to the biological molecular machines that are the essential agents of movement in living organisms. These biological molecular motors are typically complex protein assemblies[1] and hence are based on a very generous interpretation of the term "molecular".

In 2010, the groups of Wang and Boldyrev found that the lowest energy form of B_{19}^- is a beautiful ring structure with two planar π-aromatic systems nested inside each other.[2] The inner fragment, a pentagonal six-atom group sharing two π electrons, is surrounded by a periphery of thirteen boron atoms that share a further ten π electrons (Figure 1 a). More recently, Jiménez-Halla and colleagues reported that B_{19}^- is a "molecular Wankel motor".[3] The structure of the B_{19}^- double-ring allows the nearly barrier-free rotation of inner and outer rings with respect to each other. In-plane internal rotation was initially discovered in borocarbon wheels by Erhardt et al.,[4] though none of the reported forms are the lowest energy structures.[5]

In 1988, Anderson and co-workers found that the mass distribution of B_n^+ clusters from laser ablation showed numerous "magic numbers" in the range $n = 1$–20. In particular, collision-induced dissociation experiments indicated the presence of two "magic" clusters: B_5^+ and B_{13}^+.[6] Anderson and co-workers originally postulated that B_{13}^+ had a filled icosahedral structure. However, in 1996 Ricca and Bauschlicher reported a planar C_{2v} form as the ground state structure of B_{13}^+, with an inner triangle enclosed in a ten-atom ring.[7] In 1998 Schleyer and co-workers confirmed the findings of Ricca and Bauschlicher in their re-examination of various structures of B_{13}^+.[8] They were first to predict the fluxional behavior of the C_{2v} global minimum-energy structure of B_{13}^+. In 2000, Fowler and Ugalde concluded that the B_{13}^+ structure has a planar C_{2v} geometry containing an inner triangle, and exhibited exceptional π-aromatic character.[9] The fluxional behavior of B_{13}^+ has been described by Martinez-Guajardo et al. as the almost free rotation of the inner B_3 moiety inside the peripheral B_{10} ring.[10] Therefore, B_{13}^+ should be considered to be a molecular Wankel motor.

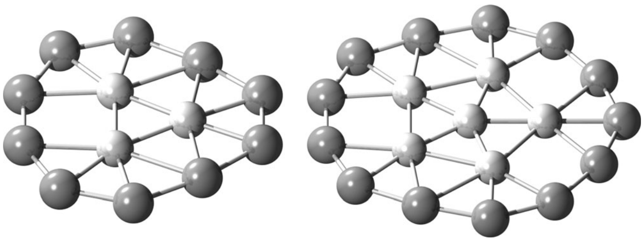

Figure 1. Structures of the global energy minima of B_{13}^+ (left) and B_{19}^- (right). All atoms are boron atoms; the inner and outer ring systems are in different shades of gray.

Despite their fluxional properties, B_{19}^- and B_{13}^+ cannot be compared with biological molecular motors, as it is unclear if the boron systems could ever work. The fundamental question that needs to be answered is: How can one trigger the rotation of such a system, or, what is the starter for a molecular Wankel motor?

Zhang and co-workers have proposed a plausible solution to this problem: They suggest to trigger the rotation of the outer ring in B_{13}^+ with respect to the inner triangular moiety by applying an external laser field.[11] Without an external field, the barrier that the B_{13}^+ system must overcome in order to rotate is 0.25 kcal mol^{-1}, and because of symmetry the rotation may occur in both directions with the same probability. If an electric field is applied in the plane of the molecule, perpendicular to the C_2 axis, the symmetry of the system is broken, and the system prefers to rotate unidirectionally: one direction is essentially barrier-free, while the opposite direction is hindered by an increased barrier; in the case of an external electric field of 2.6×10^9 V m^{-1} the barrier, 0.81 kcal mol^{-1}, is prohibitively high at low temperatures.[11] A constant motion could be driven by the application of circularly polarized light of a reasonable frequency.

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In order to exploit this important finding for a free molecule in the gas phase one needs an additional trigger: the rigid molecule could simply align itself in such way that its dipole axis coincides with the applied electric field, and no rotation of its rings with respect to each other would be possible. Zhang et al. have also found an appealing solution to this problem: The frequency of the polarized light must be chosen such that the rotation of the outer ring in B_{13}^{+} is in resonance, thus that the outer ring rotates faster than the reorientation of the rigid molecule to align its dipole moment with the external field.

Based on these insights from a thorough theoretical analysis we can expect the experimental realization of the smallest molecular motor that is known to date. It remains to be explored whether these findings—achieved for boron clusters—can be transferred to real systems, for example, by the incorporation of similar multiple rings into two-dimensional materials such as graphene. As fluxionality is not restricted to B_{13}^{+} and B_{19}^{-}, the proposed electromagnetic starter of the B_{13}^{+} wankel motor may also serve as a starter for exploring these fascinating phenomena in nanotechnological systems. Finally, this starter is unique to molecular motors because it does not need electronic excitation, that is, it operates adiabatically. This helps to reduce energy dissipation.

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