Facilities and instrumentation used: EMR program, 15/17 Tesla Transmission Spectrometer, 371GHz Microwave Source.


Baird’s rule predicts that cyclic molecules with \(4n\) \(\pi\)-electrons \((n = \text{positive integer})\) should be aromatic in the triplet state; aromaticity implies complete delocalization of the two unpaired electron spins associated with the \(S = \frac{1}{2} + \frac{1}{2} = 1\) (triplet) state and an undistorted planar ring system. Unfortunately, efforts to realize such ring systems have been stymied by their tendency to distort into structures favoring a fully spin-paired singlet \((S = 0)\) ground state, with a large energy gap to the excited triplet state.

This work demonstrates that the elusive benzene diradical dianion can be stabilized through creation of an unusual metallo-ligand that enforces a tightly constrained inverse sandwich structure, with a metal ion (orange in the Figure) on each face of the central ring system. The benzene dianion possesses two additional electrons in the \(\pi\)-system, i.e., a total of \(6 + 2 = 8\) \(\pi\)-electrons. High-field EPR measurements were then employed in which the metal ions are non-magnetic yttrium(III), revealing paramagnetic signals consistent with a triplet \((S = 1)\) benzene diradical at temperatures down to 5 K. Meanwhile, X-ray diffraction finds aromaticity, consistent with Baird’s rule.

This fundamental research demonstrates how molecular symmetry, rigidity and even magnetic exchange coupling can be leveraged to preferentially stabilize and study a desired electronic/magnetic state in an organic molecule.