

## DIRADICALS AND SINGLET DIRADICALS

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Electronic structure of singlet diradicals with Kekulé structures has attracted significant attention. Diradical character of different classes of hydrocarbons, including zethrenes [1], and polyacenequinododimethides [2] was investigated using theoretical methods. On the other hand, the question whether Kekuléan system can exist in a triplet ground state was examined less extensively. The only known Kekuléan hydrocarbon whose triplet ground state has been determined experimentally is 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene [3]. It has been shown, in a recent paper, that some Kekuléan fluoranthenes are diradicals. In the energetically less favorable singlet state these hydrocarbons exhibit pronounced diradical character [4]. In the present work we are concerned with a series of azulene-like homologues, where the number of hexagons  $h = 0 - 8$ . A detailed electronic structure study of singlet and triplet states of the series members was performed using the B3LYP and complete active space (CAS) methods (Fig. 1). According to the results obtained at the B3LYP level of theory using the unrestricted symmetry-broken (USB) method, the singlet-triplet splitting for the members of the series with three and more hexagons is quite small, and in addition, four members of the series were found to be diradicals, implying that their ground state is a triplet. The CASSCF calculations revealed that higher members of the series of the azulene-like molecules with six and more hexagons are diradicals. In addition, the USB and CASSCF results showed that singlet states of these hydrocarbons exhibit pronounced diradical character. This situation is a result of a tendency of azulene-like molecules to delocalize their-electrons, thus taking up diradical structures, and achieving aromatic stabilization. This implies that aromatic stabilization is stronger than destabilization due to unpaired electrons. Even in the singlet state, these hydrocarbons show a pronounced diradical character, and their structures are best presented with that of singlet diradicals. Such structures provide a possibility for an electron pair to occupy different parts of space, and allows for achieving aromatic stabilization.

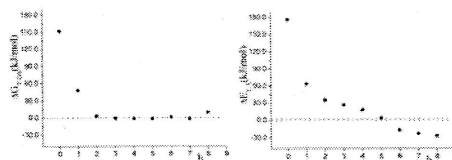


Fig. 1. Dependence of the singlet-triplet gap obtained at the B3LYP/6-311G(d,p) level (GT-OS, left), and CASSCF/6-311G(d,p) level (ET-S, right) on the number of hexagons ( $h$ ) of azulene-like molecules

### References

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