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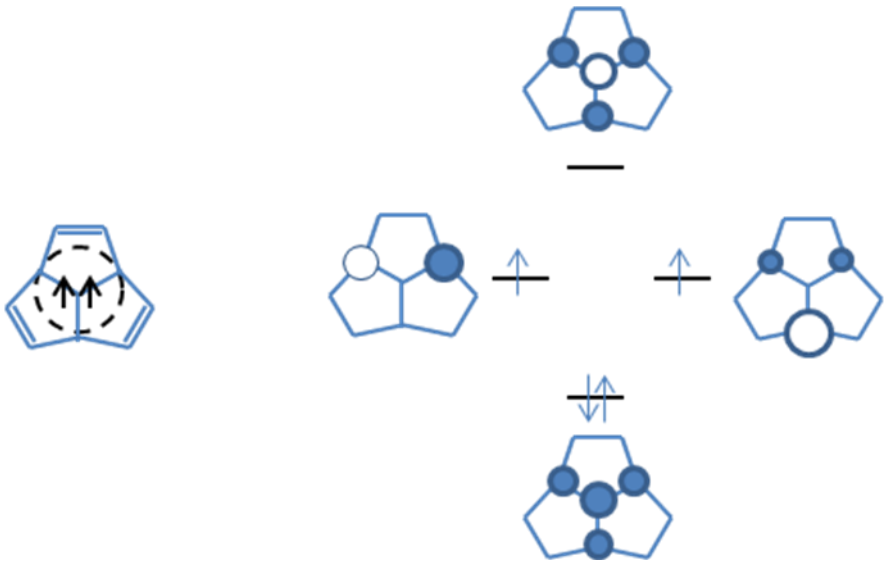
"Towards experimental determination of conical intersection properties: Twin State model and Comparison with bound excited states"

Dianion and the lowest triplet of acepentalene with high symmetric C_{3V} configuration.

The lowest triplet state has a high symmetric C_{3V} configuration with a three double C=C bonds between peripheral HC groups according to the previous DFT and our CAS calculations (Figure 2, Ic and IIc). The central trimethylenemethane fragment has a high-conjugated triplet state with a three allyl type resonances (Sup3. Figure 1a):



a. **b.**

Sup3. Figure 1 a. Schematic electronic structure of the T_1, b. Highest occupied MO, lowest unoccupied MO and two single occupied non-bonding MOs.

Two unpaired electrons of T_1 occupy the two low-lying degenerate non-bonding orbitals (Sup3. Figure 1b). It provides the stable C_{3V} configuration of acepentalene T_1. This effect has the same origin as in the parent trimethylenemethane[1]. In the dianion of acepentalene two electrons are added, so that four electrons occupy these two non-bonding orbitals. It keeps the stable C_{3V} configuration also for dianion (Figure 2, Ie and IIe).

[1]W.T. Borden, *J. Amer. Chem Soc.*, **1975**, *97*,2906; E.R.Davidson and W.T. Borden, *J. Amer. Chem Soc.*, **1977**, *99*,2053.

Mono-anion $\mathbf{I}^{-1}/\mathbf{II}^{-1}$ in C_{3V} configuration has a degenerate pair of HOMOs occupied by three electrons, which is an obvious Jahn-Teller case.