The bonding nature of some simple sigmatropic transition states from the topological analysis of the electron localization function

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It is shown that the topological analysis of the electron localization function (ELF), a measure of the local Pauli repulsion, is a useful tool to describe the bonding nature of transition structures of simple pericyclic processes. In this work, we have revisited the [1s,3a]hydrogen, [1a,3s]methyl, and [1a,3s]fluorine simple sigmatropic rearrangements in the allyl system. Results based on the integrated densities over the ELF basins and their related properties at the B3LYP/6-311++G(d,p) level of theory showed explicitly a delocalized structure for the antarafacial (Cs hydrogen rearrangement, a two radical interaction for the methyl suprafacial (C2) migration, and a pair-ion interaction for the fluorine suprafacial (Cs) transfer. Results on these well-studied systems confirm the topological analysis of the ELF as a useful descriptor for the study of bonding structure of pericyclic transition states. In this context, the ELF analysis is shown to be a complementary value to the Woodward-