

*Electronic Supplementary Information for*

**Bimolecular Hydrogen Transfer in Phenalene by a Stepwise Ene-like Reaction Mechanism**

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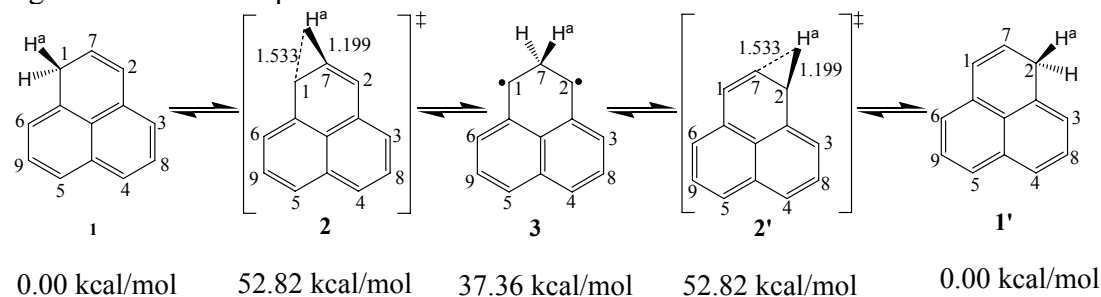
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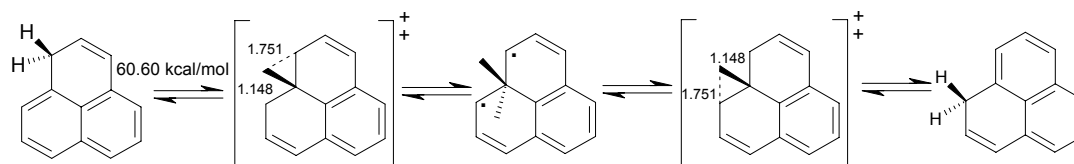
**The intramolecular hydrogen transfer process:**

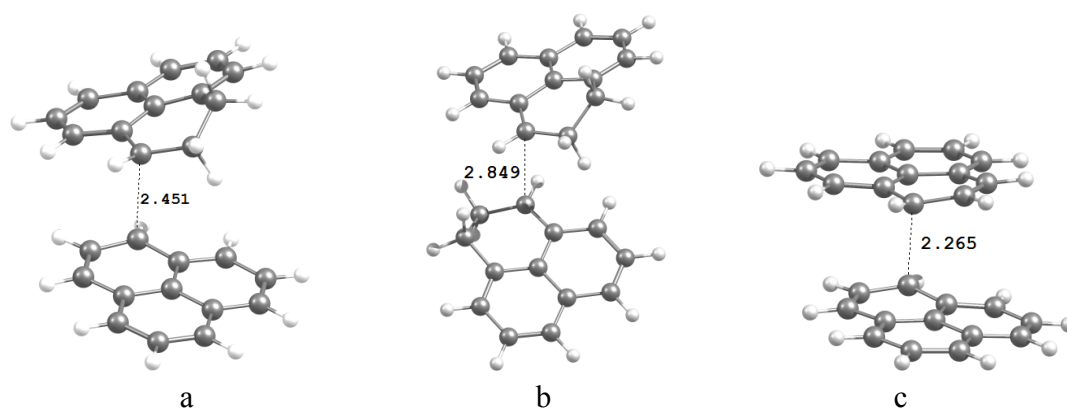
The phenalene reactant first undergoes suprafacial [1,2] hydrogen shift from C1 to C7 yielding a biradical intermediate that in turn undergoes another [1,2] hydrogen shift from C7 to C2 as depicted in Scheme S-1. The UB3LYP calculated barrier from the reactant to the intermediate is very high at 52.82 kcal/mol in terms of enthalpy. It is noted that the intermediate **2** has been detected during the epimerization of naphthocyclopropane (R. M. Pagni, M. N. Burnett, H. M. Hassaneen, *Tetrahedron*, **1982**, *38*, 843-851.). In addition to pathways described in Scheme 2, another [1,3] hydrogen shift from C1 to C6 was described in Scheme S-2. The corresponding barrier is 60.60 kcal/mol. The TS structure was optimized at UB3LYP/6-31G(d,p) level. The electronic energies were calculated by UB3LYP/6-311+G2dp/UB3LYP/6-31G(d,p). The thermal corrections were calculated by UB3LYP/6-31G(d,p).

**Scheme S-1.** The [1,3] hydrogen shift by the proposed two-step mechanism corresponding to a biradical intermediate. The optimized C-H distances are listed in angstroms. The enthalpies relative to **1** are listed below the structure number.

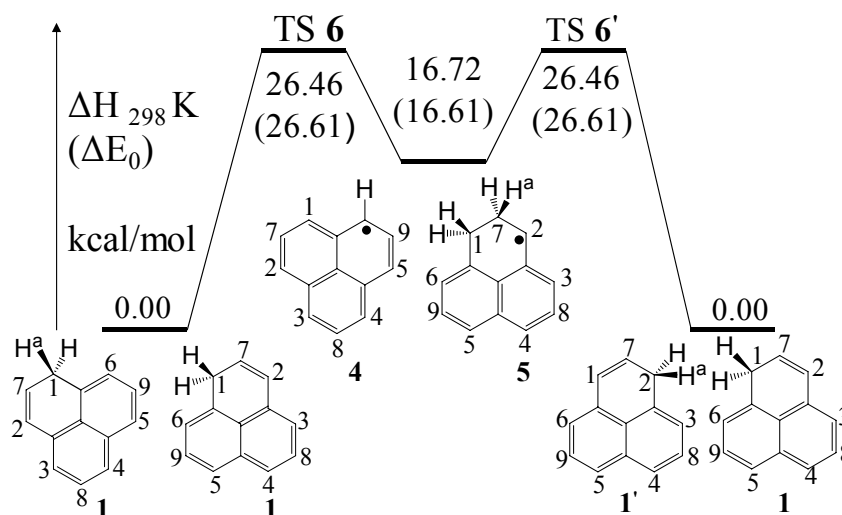


**Scheme S-2.** The [1,3] hydrogen shift by the proposed two-step mechanism corresponding to a biradical intermediate. The optimized C-H distances are listed in angstroms. The relative enthalpies are listed below the structure number.





**Figure S-1.** The structures of the transition state connecting to (a) the intermediacies 4, 5 and dimer 7; (b) the intermmmediacies 5 and 9; (c) the intermmmediacies 4 and 9.



**Fig. S-2.** The energies of the bimolecular hydrogen transfer reaction and the competitive dimerization reactions calculated by M05-2X/6-311+G(2d,p)//M05-2X/6-31G(d,p).

**Author lists truncated for ref. 11:**

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