Intermolecular-type conical intersections in benzene and catechol dimers

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Abstract

The equilibrium geometries of the ground and first electronic excited states as well as the radiationless deactivation channels of catechol and benzene in their monomer and dimer configurations were investigated using the standard linear-response and the spin-flipped TDDFT together with the ωB97X-D3 exchange-correlation functional, as well as by the multireference CASSCF methods, considering the minimally augmented ma-def2-TZVPP and the 6-31G** basis sets. Intermolecular-type CI geometries can be formed between the two monomers, where both aromatic rings show planar deformation and a weaker, approximately 1.6-1.8 Å long, C-C bonds are formed between the two monomers, with multiple orientation configurations of the monomers relative to each other. It was also shown that, these, intermolecular-type CIs are energetically more favorable than CIs containing only one deformed monomer. The validity of the dimer-type CI geometries obtained by SF-TDDFT was confirmed by the CASSCF method.

Figure 1. The S0/S1 conical intersection geometries of of benzene.

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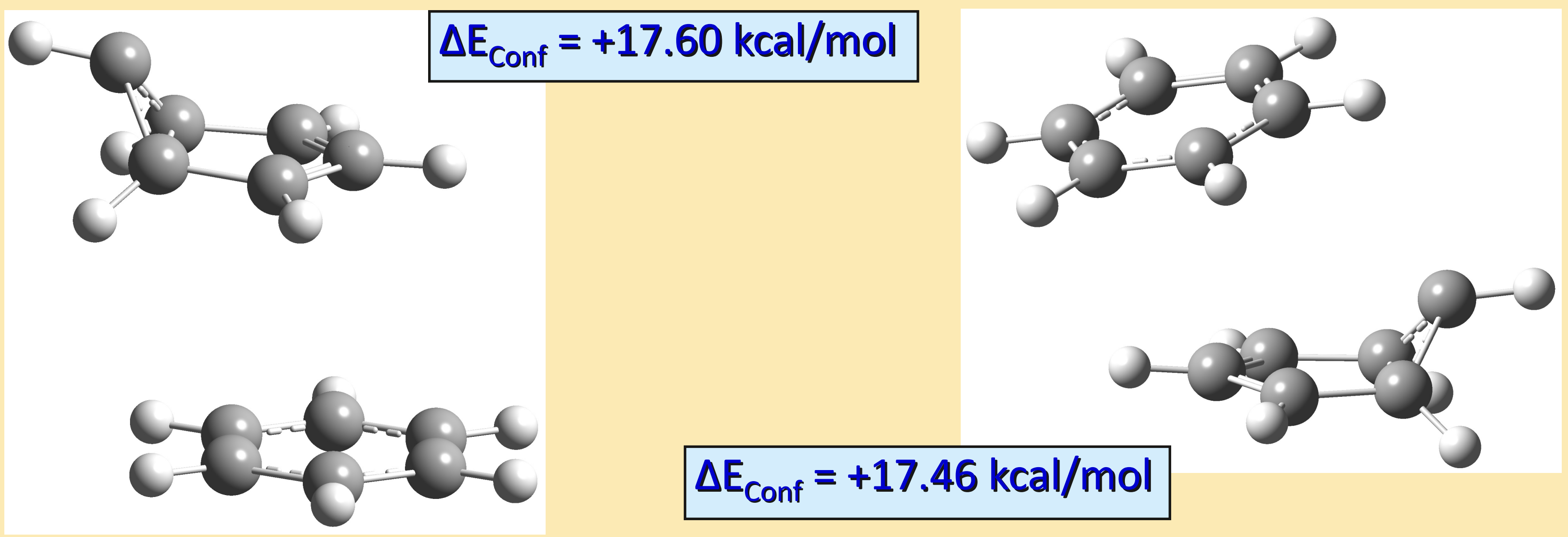
Monomer-type S0/S1 CIs:



Dimer-type S0/S1 CIs:

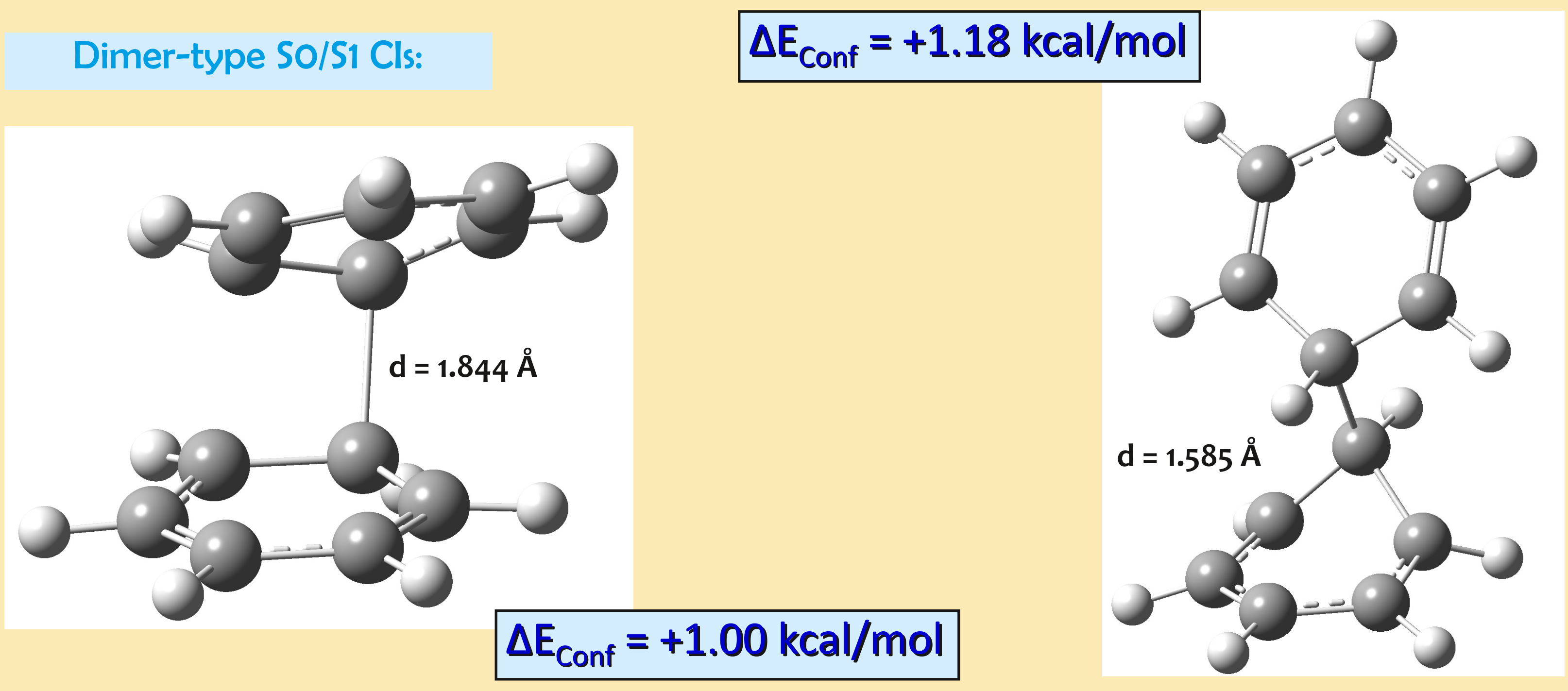
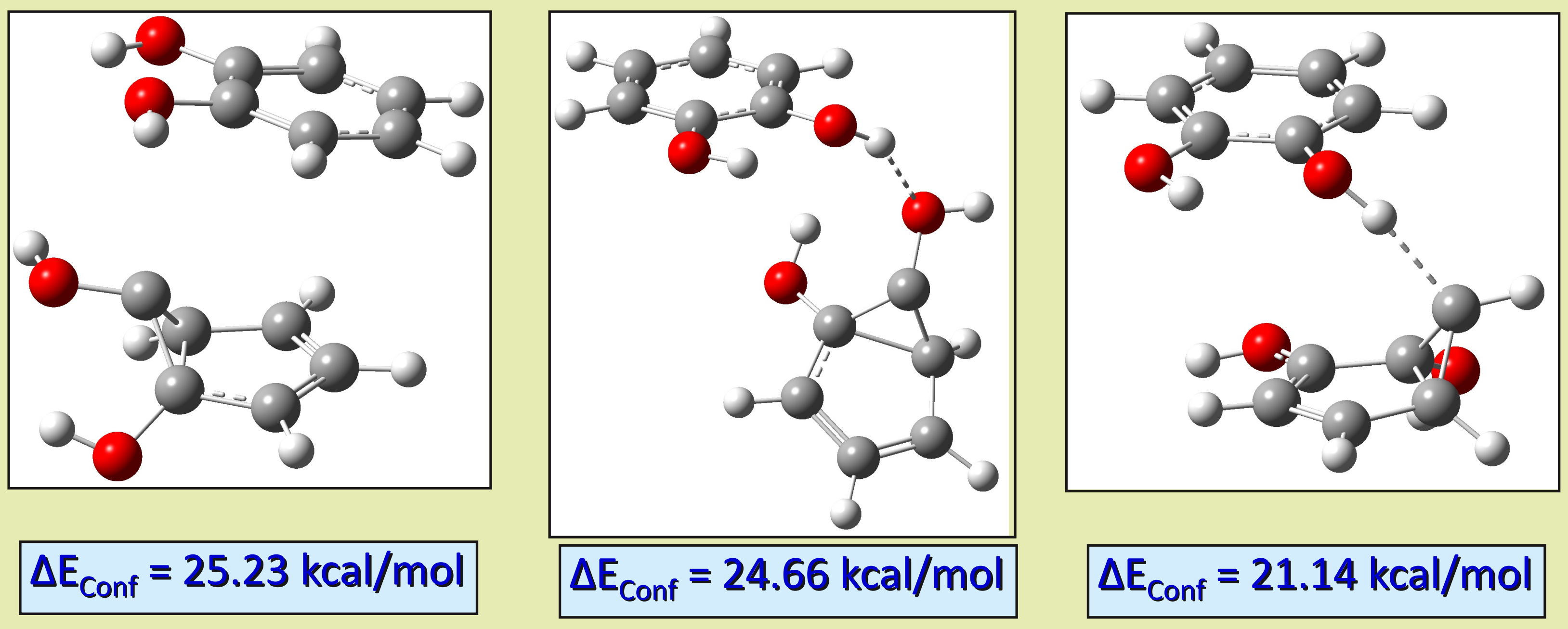


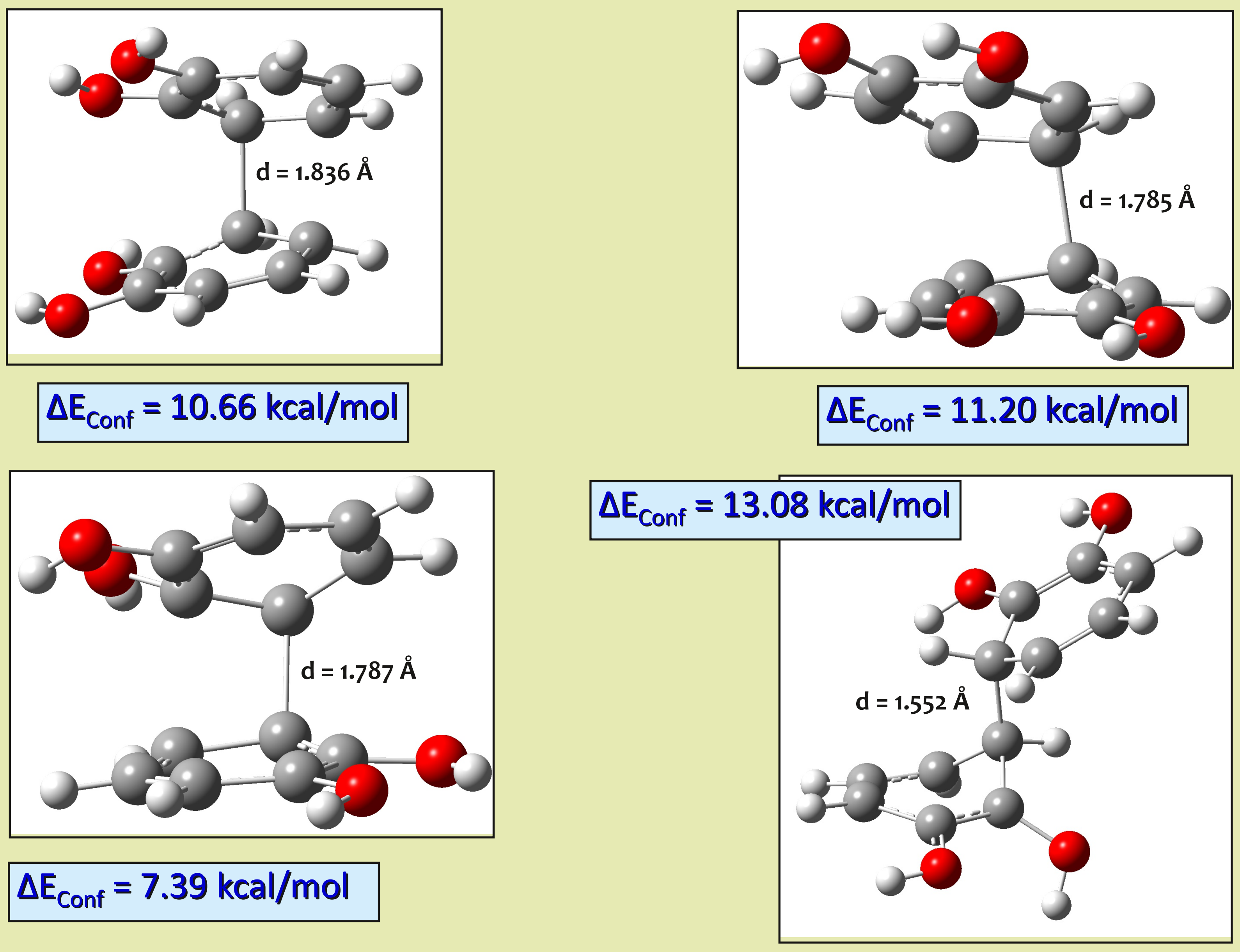
Figure 4. The S0/S1 conical intersection geometries of catechol.

Monomer-type S0/S1 CIs:



Dimer-type S0/S1 CIs:

Results published in: A. Bende, A.-A. Farcaş, A. Falamaş, A. Petran, *Phys. Chem. Chem. Phys.*, **2022**, *24*, 29165.



Methods:

- The equilibrium geometries of the ground and first excited electronic states of benzene and catechol were computed considering the ωB97X-D3/ma-def2-TZVPP/CPCM(without solvent or Acetonitrile) method.
- The S_1 electronic excited states (λ_{S1}-s) were computed using the equation-of-motion coupled cluster built with the domain-based local pair natural orbitals (DLPNO-STEOM-CCSD) method [1,2] implemented in Orca [3].
- The conical intersection (CI) points were localized through the spin-flipped TD-DFT [4,5] method considering the ωB97X-D3/ma-def2-TZVPP/CPCM(without solvent or Acetonitrile) level of theory and the Tamm–Dancoff approximation [6].

Figure 2. The S0/S1 conical intersection geometries of of benzene (cont.).

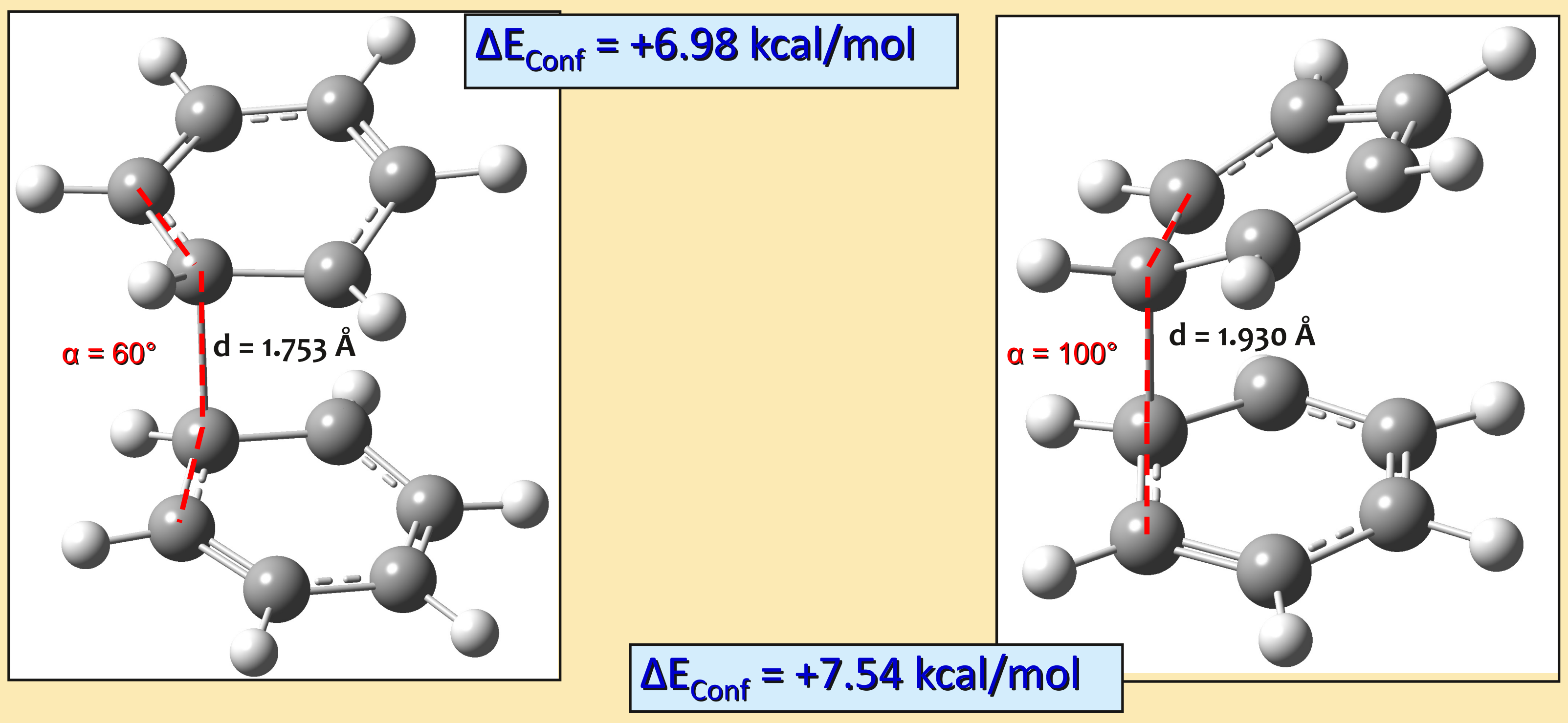


Figure 3. The ground and S1 state dimer equilibrium geometries of benzene.

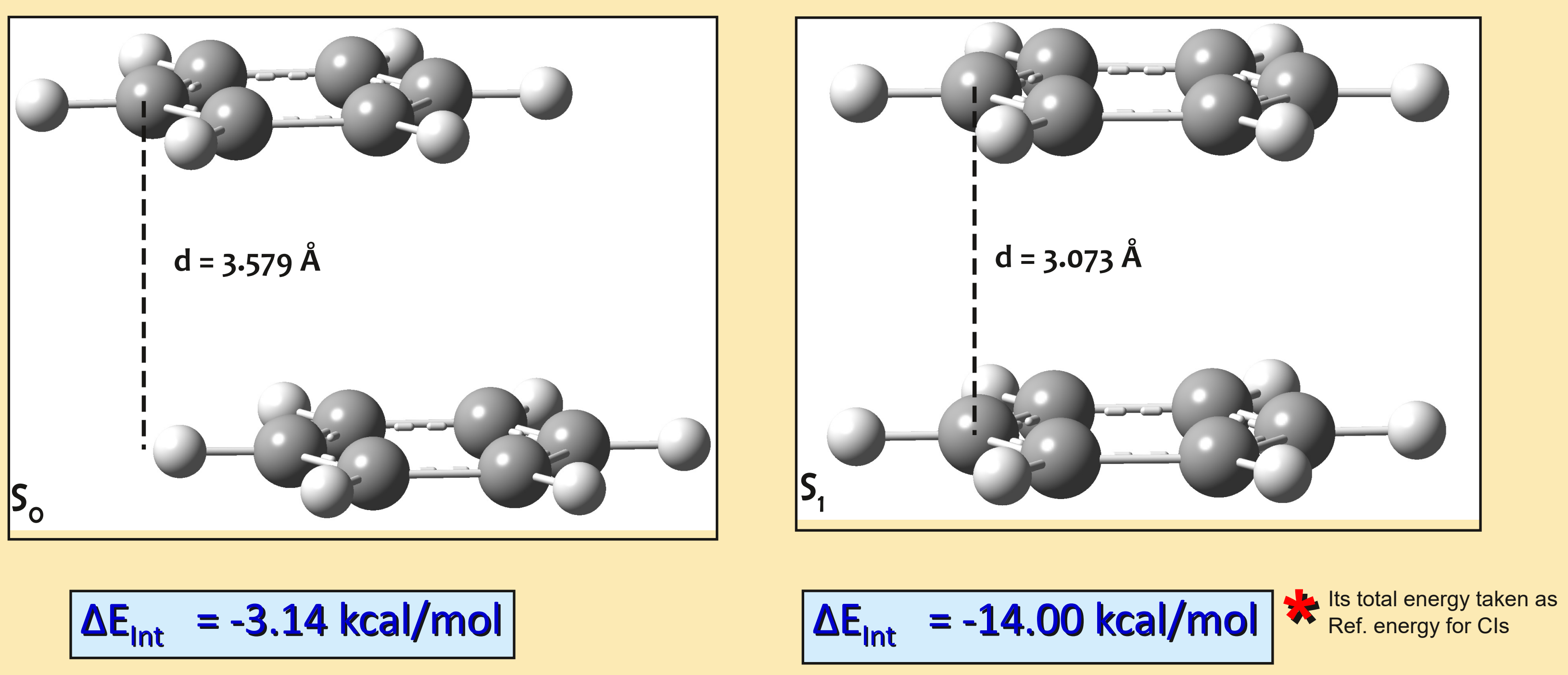
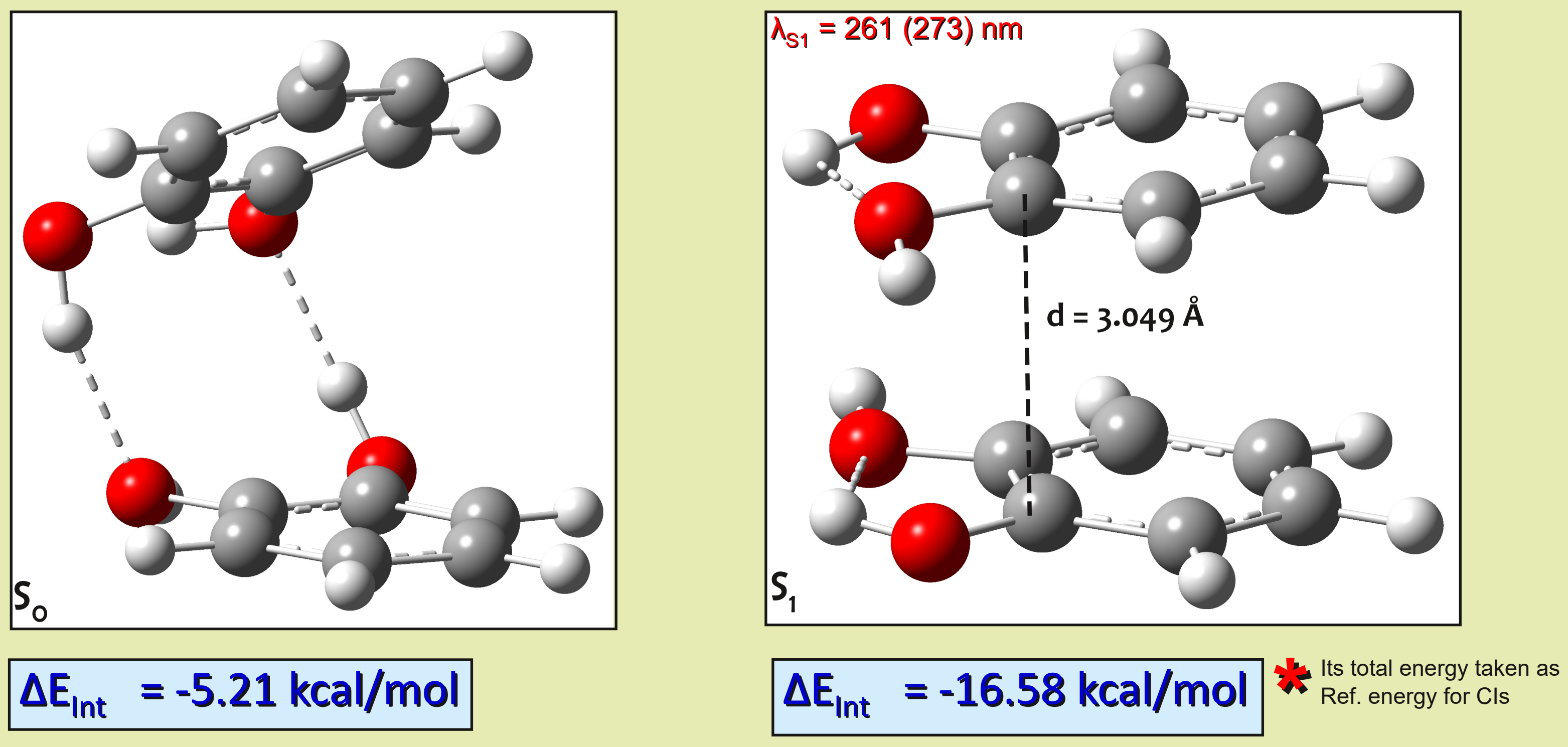


Figure 5. The ground and S1 state dimer equilibrium geometries of catechol.



Conclusions:

- Stronger intermolecular interaction energies between the monomers were found for the S1 state than for the S0 state.
- Dimer configurations in the S1 electronic state prefer the perfect stacking geometry configuration instead of shifted-stacking or H-bonded forms.
- The dimer-type conical intersection geometries are energetically more favorable than the monomer-type CI configurations.

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