

Attila Bende

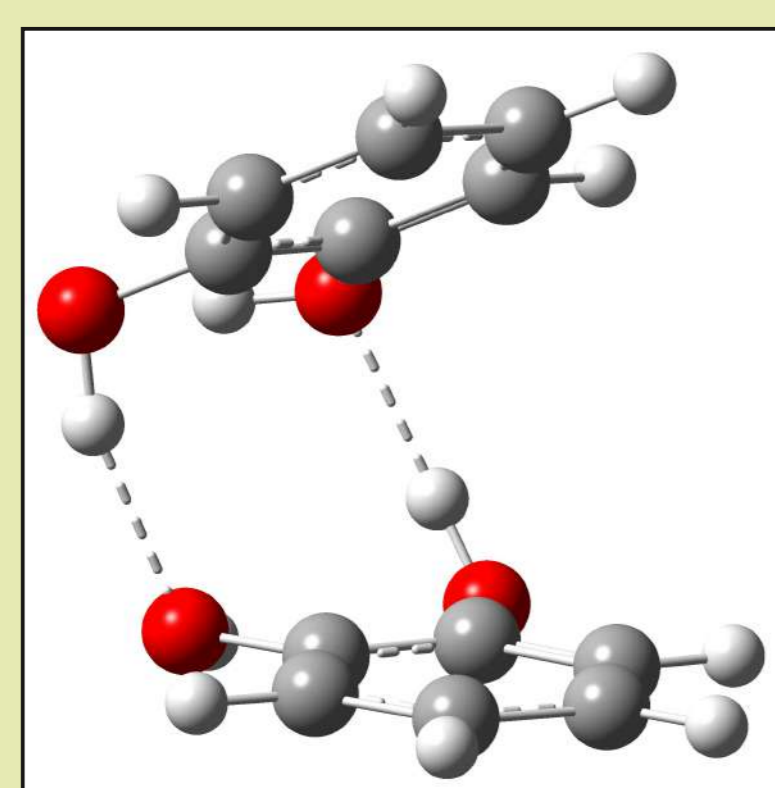
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Abstract: The non-radiative deactivation channels of the electronically excited states of the catechol were investigated by spin-flipped TD-DFT in acetonitrile solvent environment. Several conical intersection (CI) geometries were identified and their energetic parameters were compared to find the most favorable deactivation pathway. Two different families of CI geometry configurations were found, the first case is strongly related to the monomer geometries and their deformations (benzene-like CI conformations), while the second family is characteristic for the “dimer-like” CI configurations, which give lower barriers for the efficient radiationless deactivation of the electronic excited states. Furthermore, the deprotonated and radical electron configuration cases were also investigated and their radiationless deactivation pathways were compared with those found for the neutral catechol.

Method:

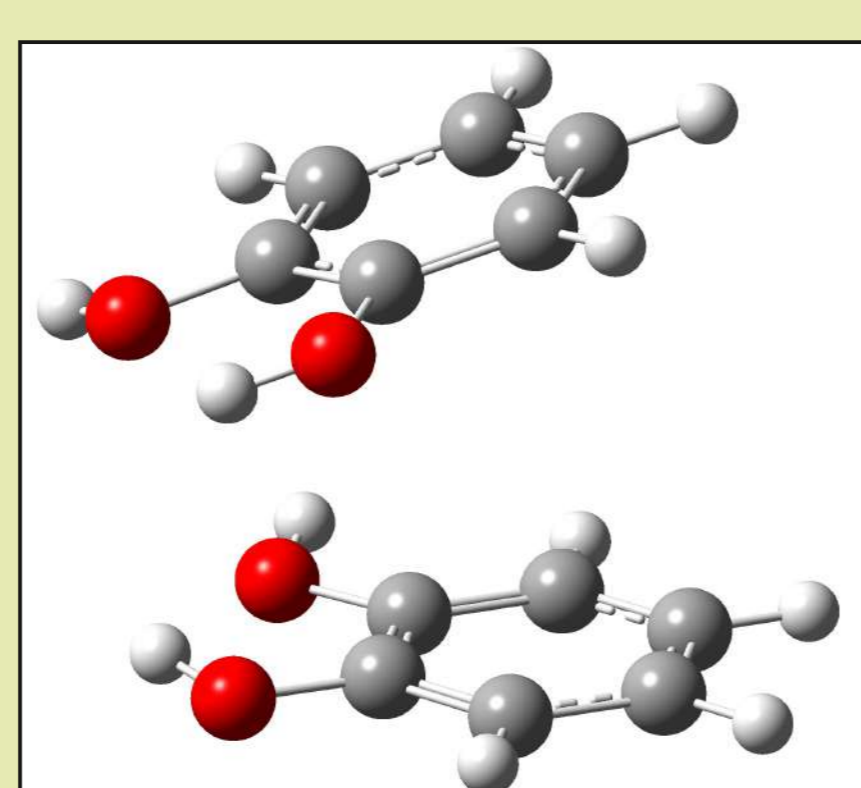
- The equilibrium geometries of the ground and first excited electronic states of catechol were computed considering the ω B97X-D3/ma-def2-TZVPP/CPCM(Acetonitrile or Cyclohexane) method.
- The S_1 electronic excited states (λ_{S_1} -s) were computed using the equation-of-motion coupled cluster built 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 ω B97X-D3/ma-def2-TZVPP/CPCM(Acetonitrile or Cyclohexane) level of theory and the Tamm–Dancoff approximation [6].

Figure 1. The ground state dimer configurations.



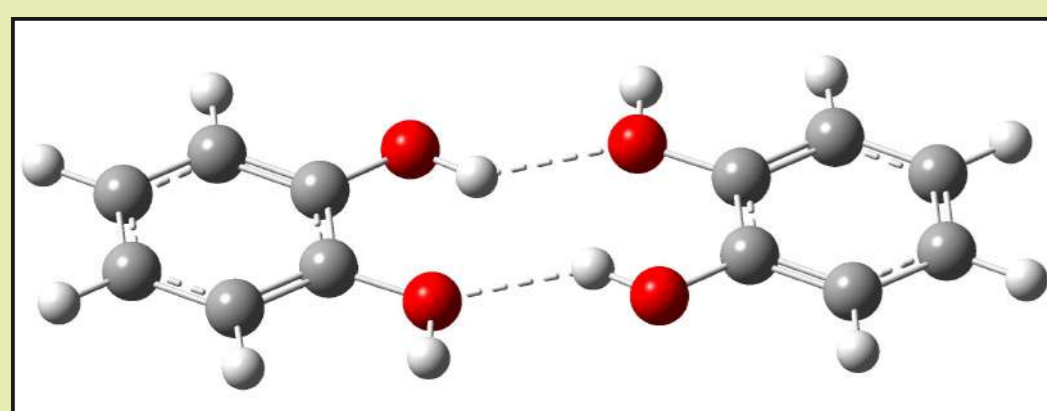
$$\Delta E_{\text{Conf}} = 0.0$$

$$\Delta E_{\text{Int}} = -5.21 \text{ kcal/mol}$$



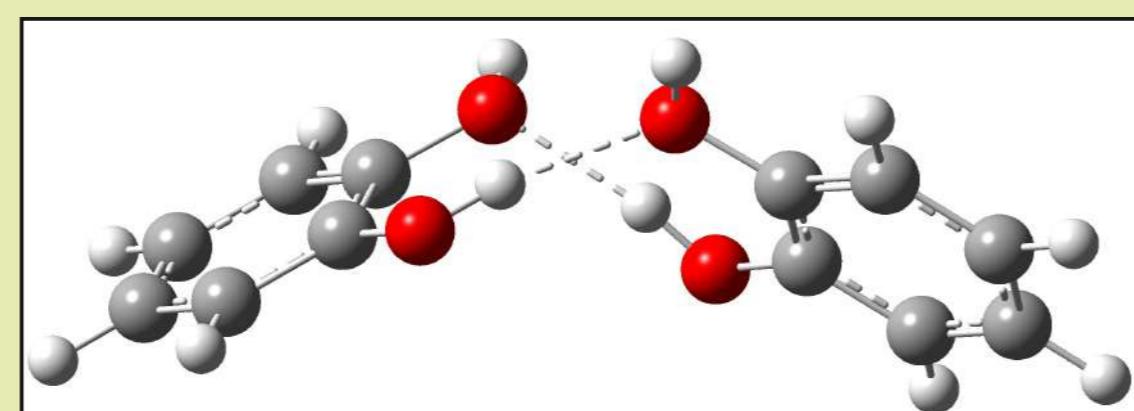
$$\Delta E_{\text{Conf}} = +1.84 \text{ kcal/mol}$$

$$\Delta E_{\text{Int}} = -9.35 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = +1.95 \text{ kcal/mol}$$

$$\Delta E_{\text{Int}} = -3.56 \text{ kcal/mol}$$

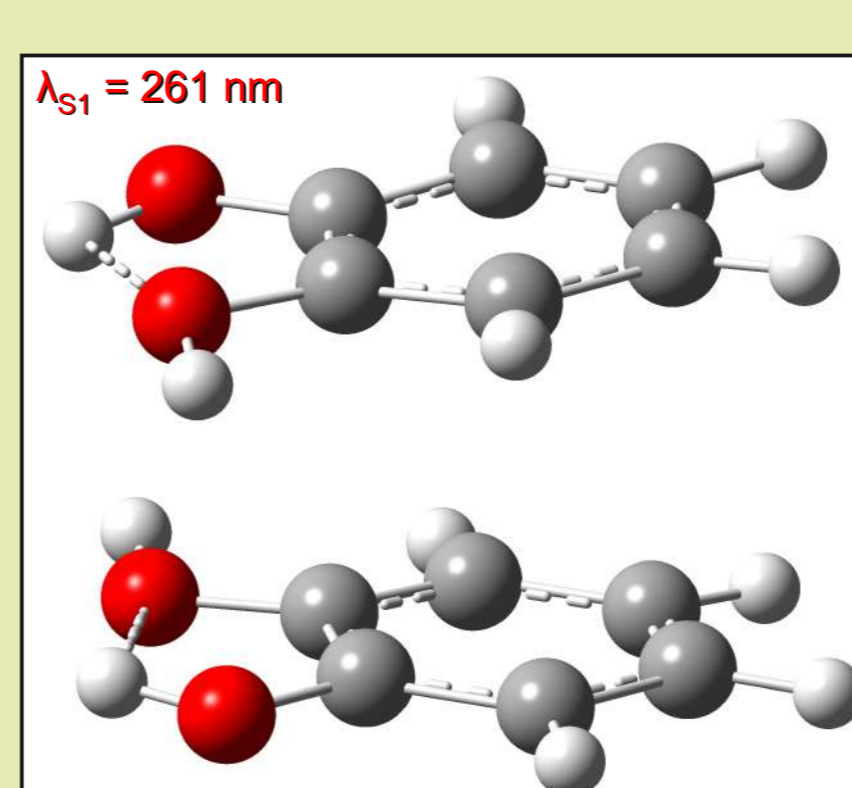


$$\Delta E_{\text{Conf}} = +0.17 \text{ kcal/mol}$$

$$\Delta E_{\text{Int}} = -5.34 \text{ kcal/mol}$$

Figure 2. The S_1 excited state dimer configurations.

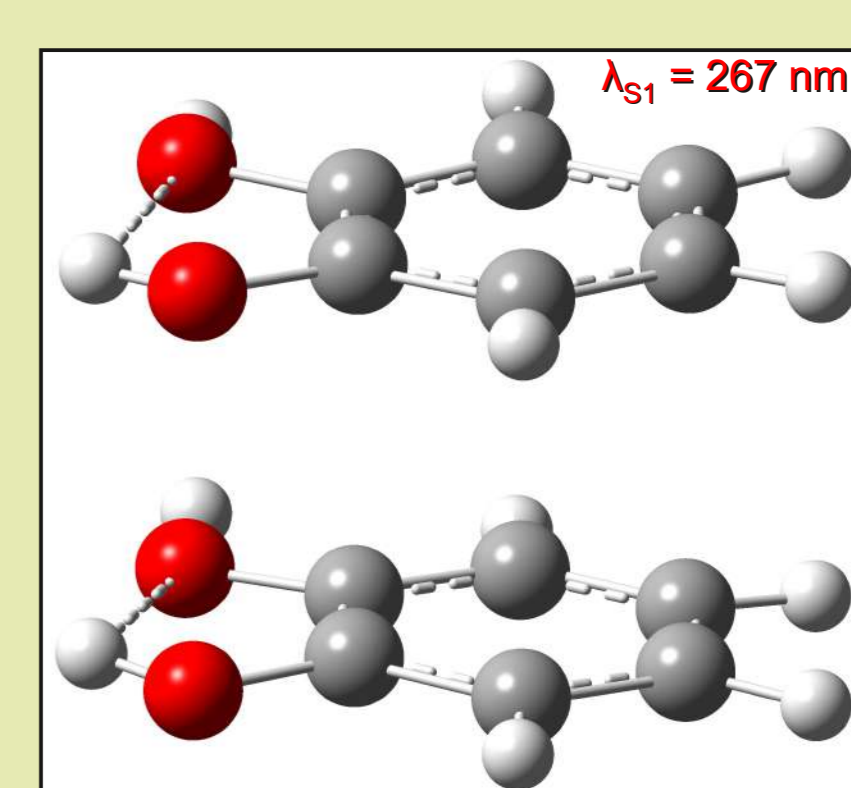
$\lambda_{S_1}(\text{monomer}) = 273 \text{ nm}$



$$\Delta E_{\text{Conf}} = 0.0$$

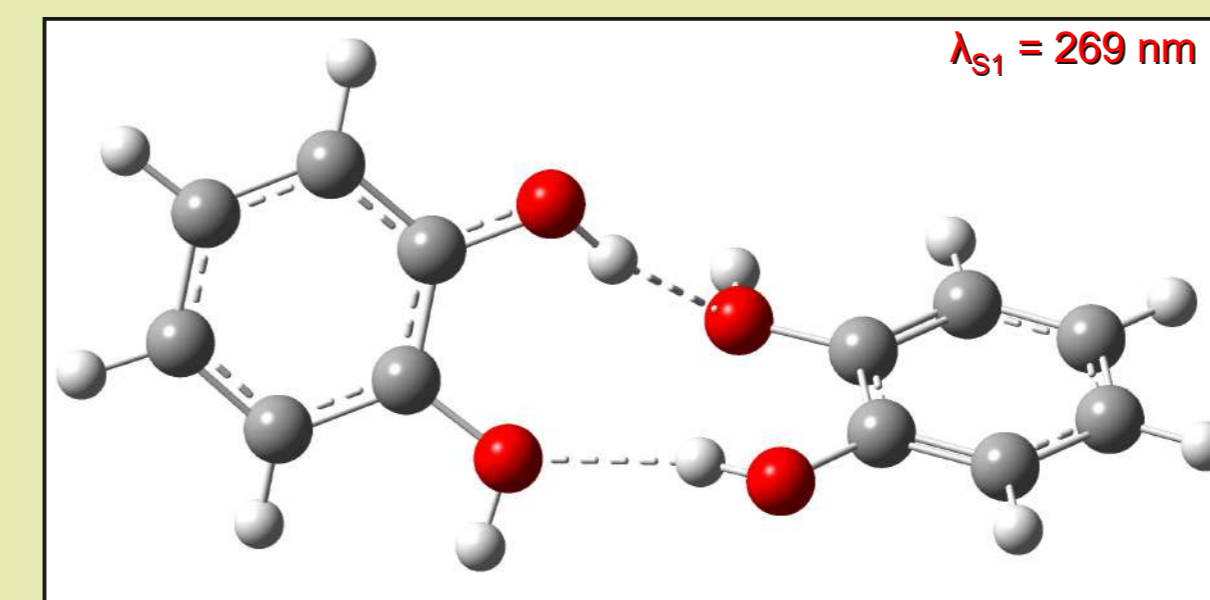
$$\Delta E_{\text{Int}} = -16.58 \text{ kcal/mol}$$

Taken as Ref. energy for CIs



$$\Delta E_{\text{Conf}} = +0.90 \text{ kcal/mol}$$

$$\Delta E_{\text{Int}} = -15.62 \text{ kcal/mol}$$

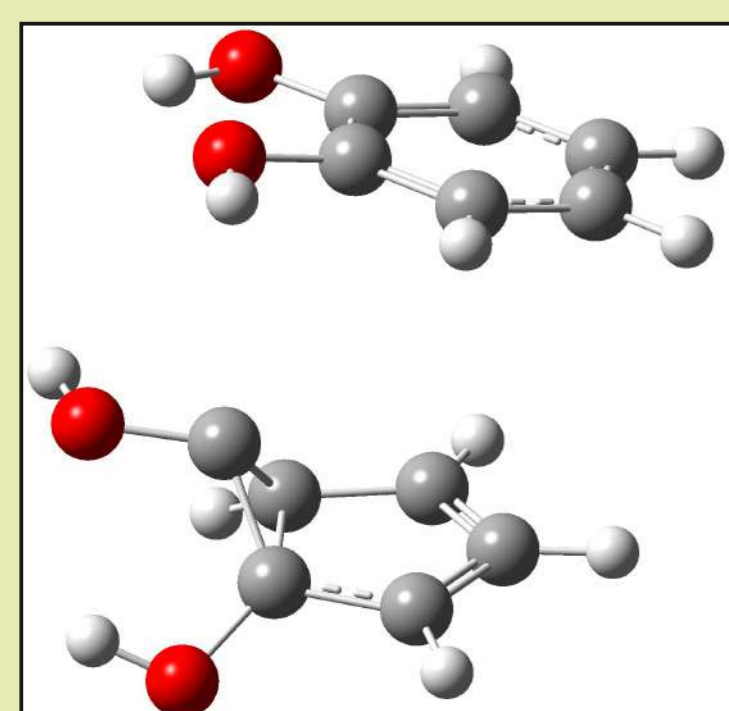


$$\Delta E_{\text{Conf}} = +8.10 \text{ kcal/mol}$$

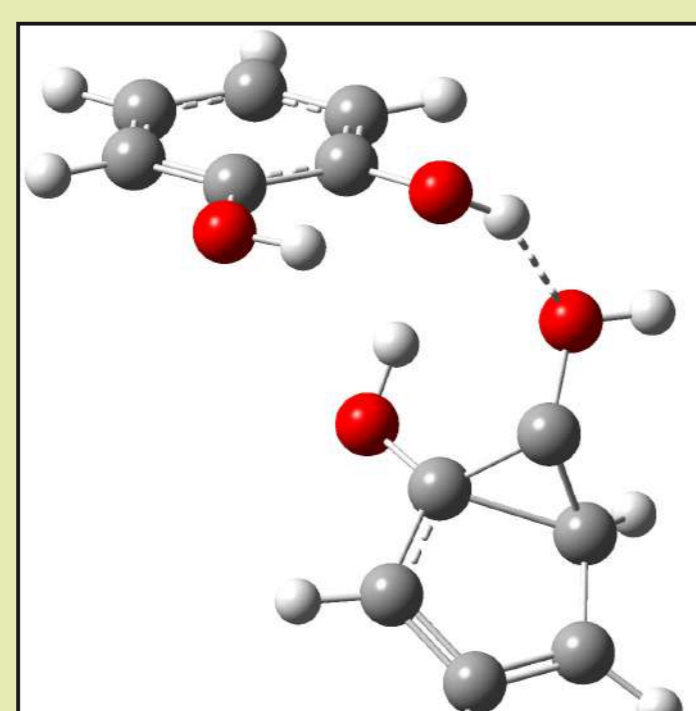
$$\Delta E_{\text{Int}} = -6.69 \text{ kcal/mol}$$

Figure 3. The S_0/S_1 conical intersection geometries.

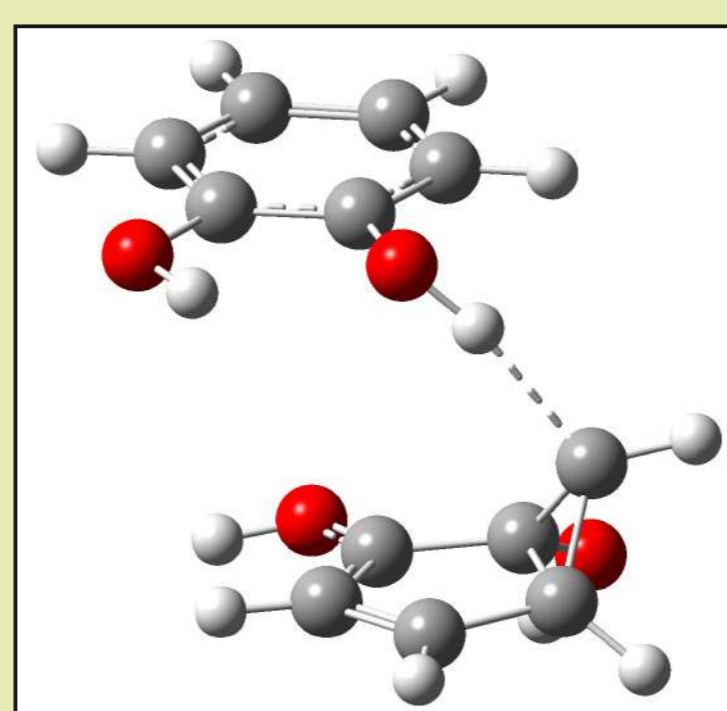
Monomer-type S_0/S_1 CIs:



$$\Delta E_{\text{Conf}} = 25.23 \text{ kcal/mol}$$

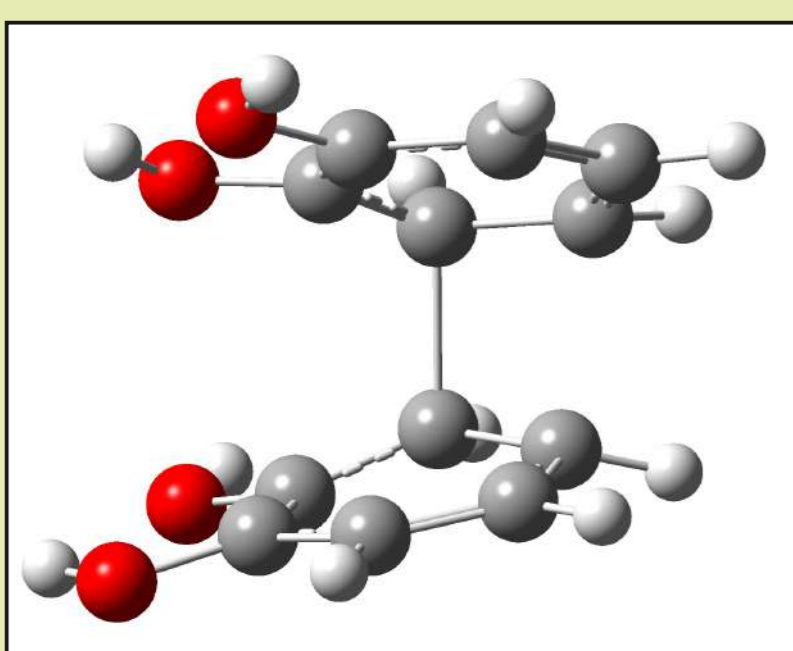


$$\Delta E_{\text{Conf}} = 24.66 \text{ kcal/mol}$$

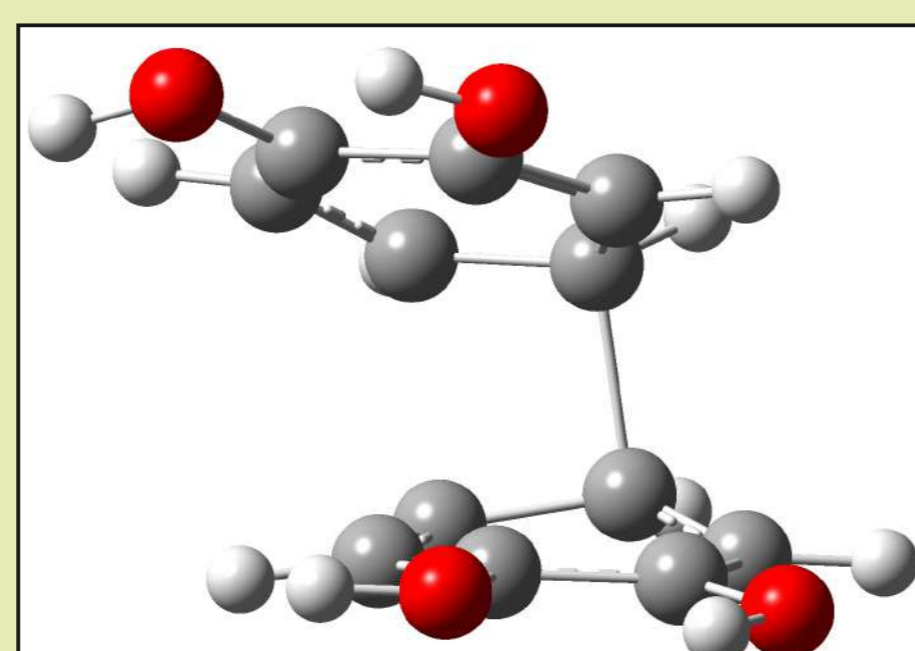


$$\Delta E_{\text{Conf}} = 21.14 \text{ kcal/mol}$$

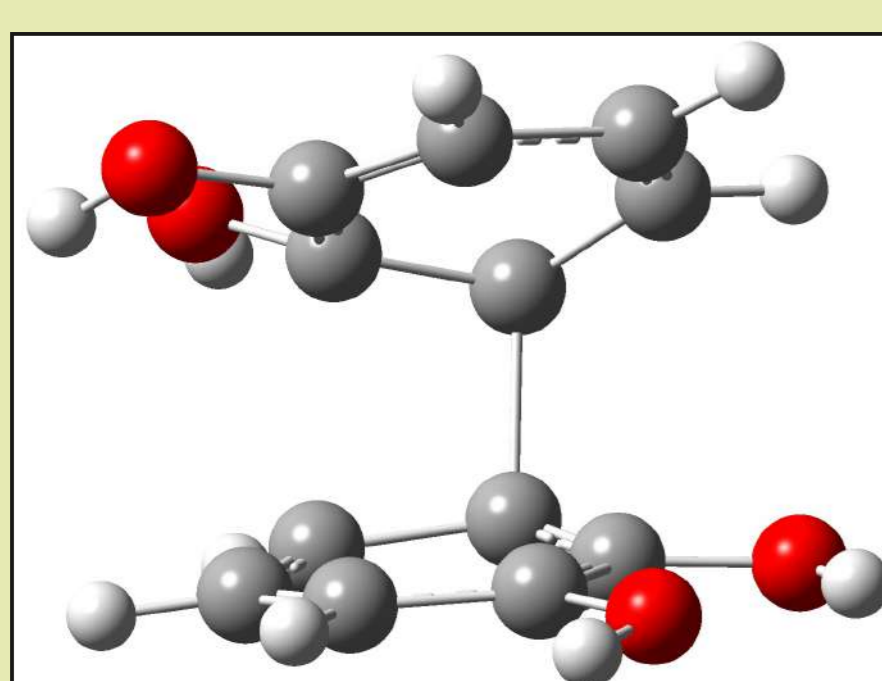
Dimer-type S_0/S_1 CIs:



$$\Delta E_{\text{Conf}} = 10.66 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = 11.20 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = 7.39 \text{ kcal/mol}$$

$$\Delta E_{\text{Conf}} = 13.08 \text{ kcal/mol}$$

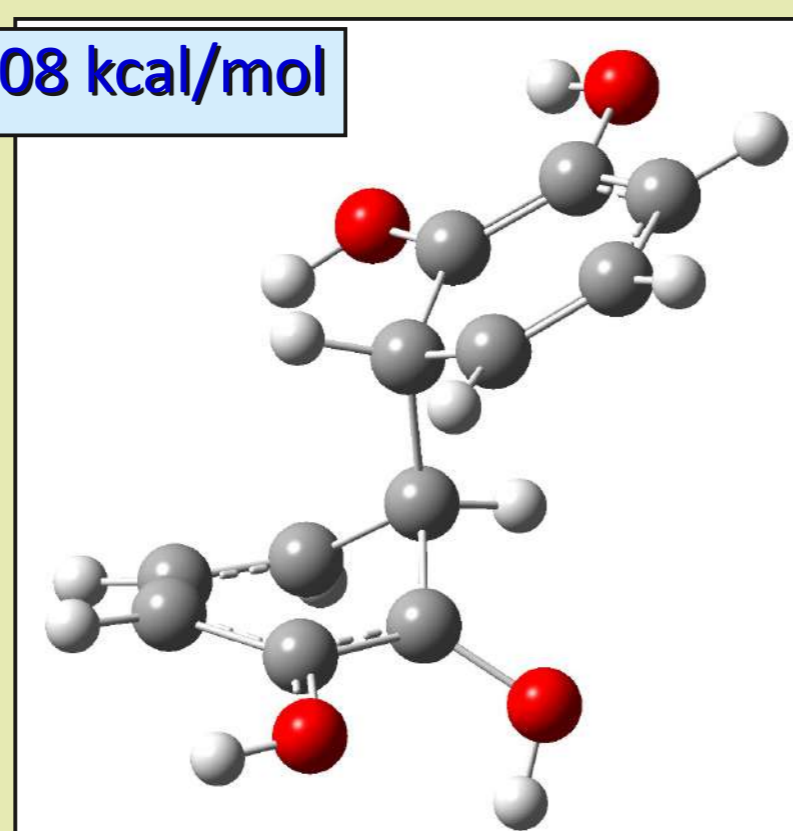
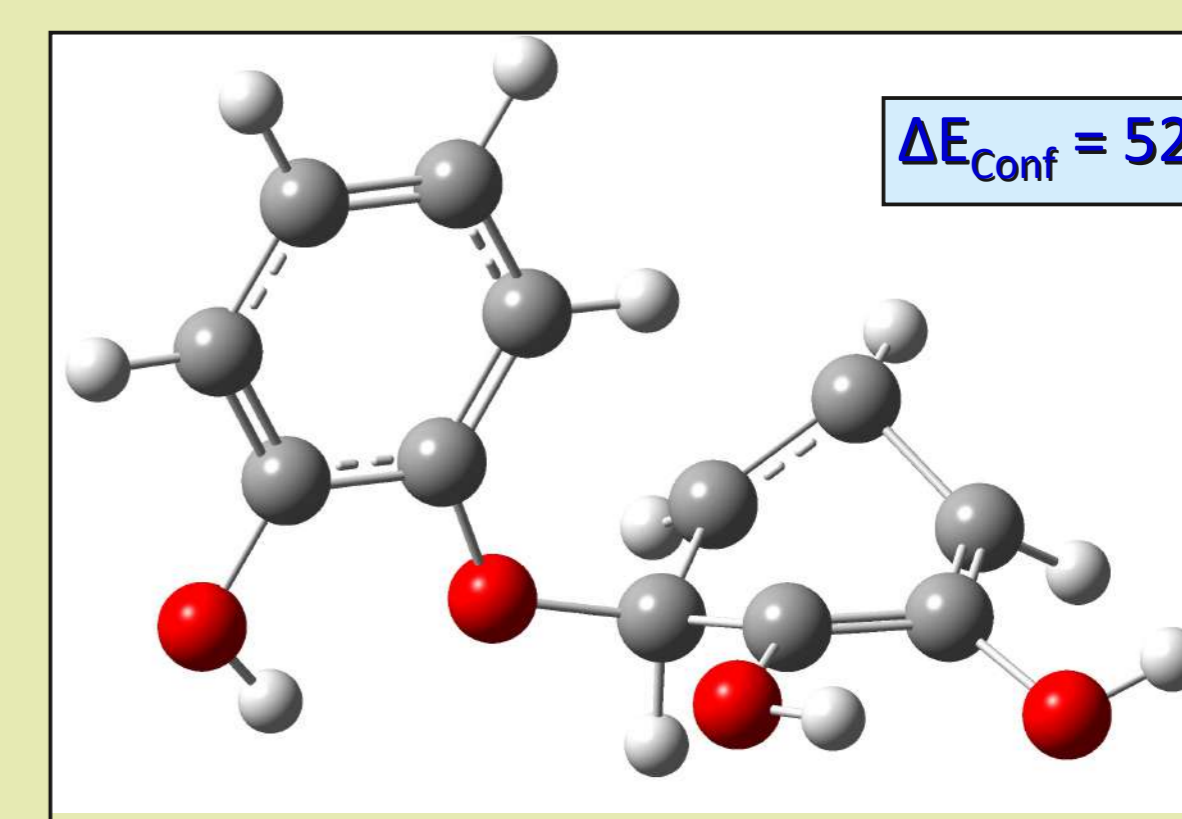
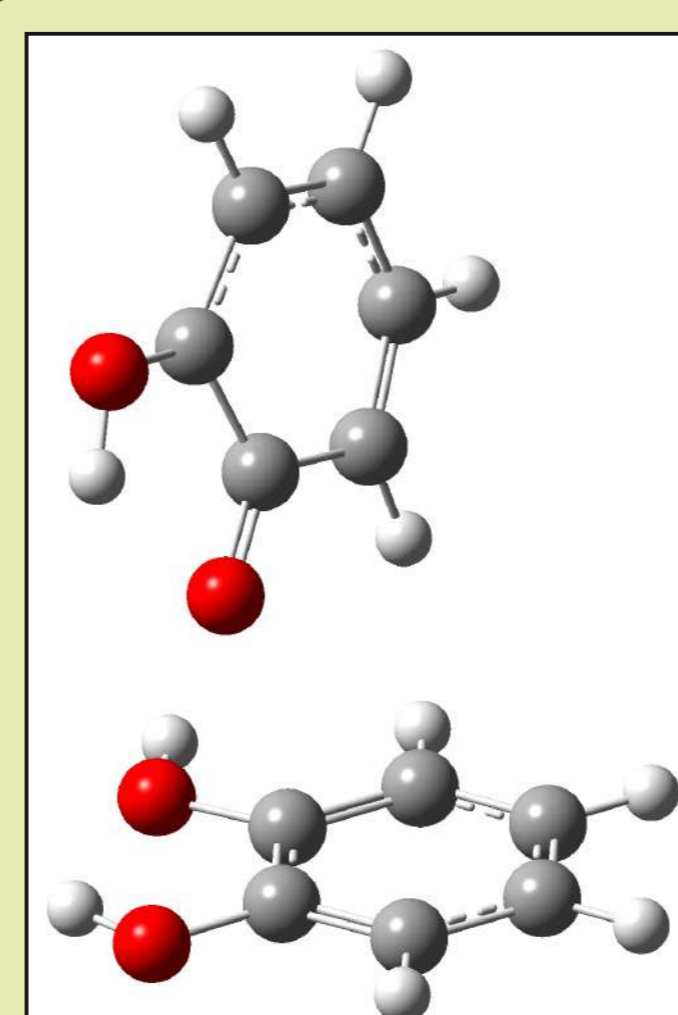


Figure 4. The S_1 equilibrium and S_0/S_1 conical intersection geometries of the deprotonated catechol.



$$\Delta E_{\text{Conf}} = 52.34 \text{ kcal/mol}$$

Conclusions:

- Stronger intermolecular interaction energies between the catechol monomers were found for the first excited electronic state.
- Dimer configurations in the S_1 electronic state prefer the stacking geometry configuration instead of the H-bonded.
- The dimer-type conical intersection geometries are energetically more favorable than the monomer-type configurations.
- Deprotonated catechol also shows dimer-type conical intersection geometry, but is energetically less favorable than for the neutral dimer.

Acknowledgement

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