Electronic Supplementary Information (ESI)

for

Controlled intramolecular H-transfer in Malonaldehyde in the electronic ground state mediated through the conical intersection of $^1n\pi^*$ and $^1\pi\pi^*$ excited electronic states

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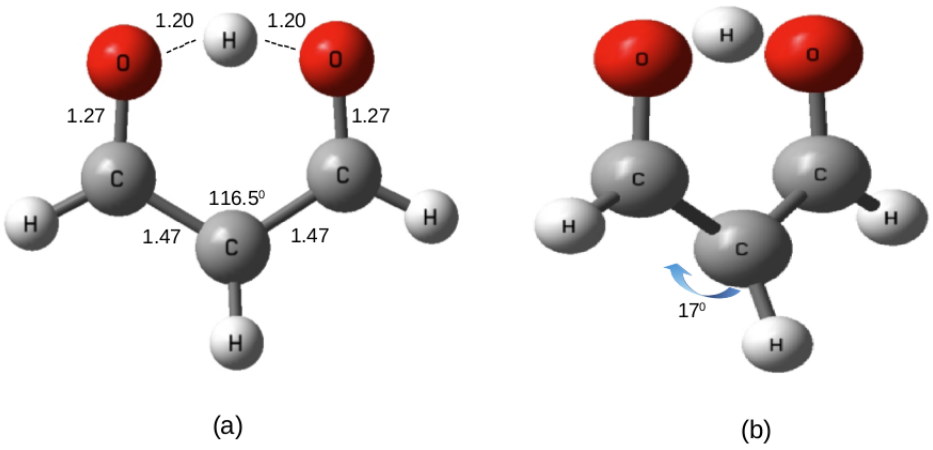

FIG. S1. The optimized geometry of hydrogen-transfer S_2/S_1 conical intersection (in two different orientations shown in a and b), computed with SA-CAS(4,4) SCF/6-31G(d) method.

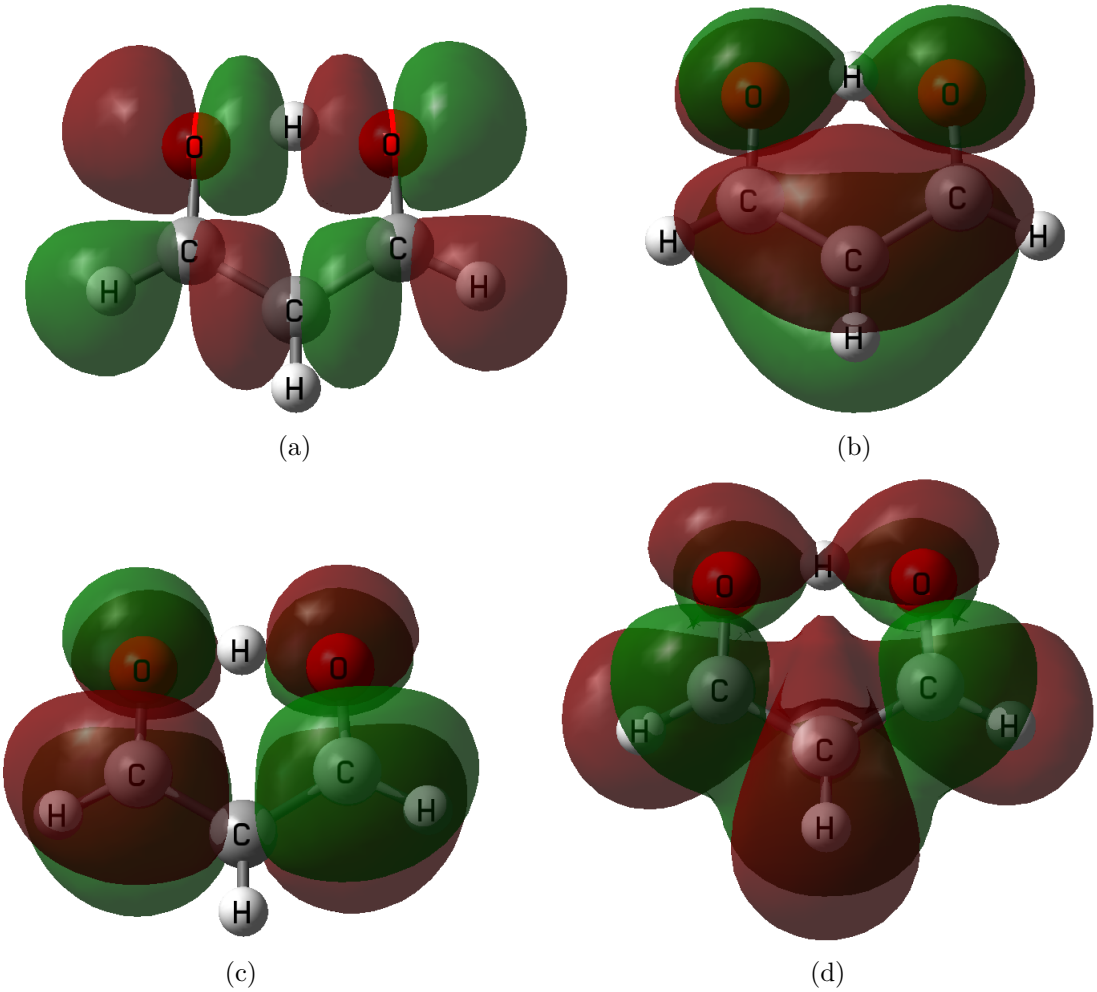

FIG. S2. The active space orbitals chosen at the CI geometry from CAS(4,4) SCF calculations. Plots in panels a, b, c and d, respectively, denote n, π, π_1^*, π_2^* orbitals.

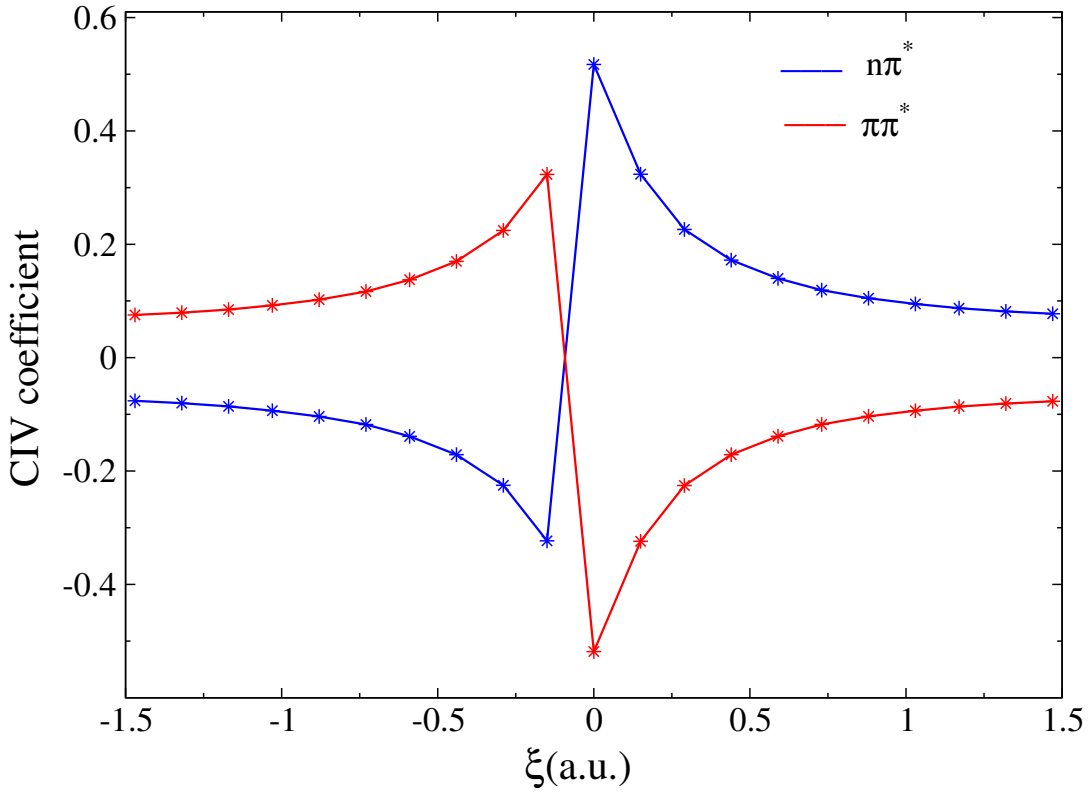

FIG. S3. The configuration interaction vector (CIV) coefficients of S_1 and S_2 electronic states along ξ. The blue and red colour asterisks are for the $n\pi^*$ (S_1) and $\pi\pi^*$ (S_2) states, respectively.

TABLE S1. Coefficients of configuration interaction wavefunctions at the conical intersection geometry calculated at the CAS(4,4) SCF level of theory. The first column represents the active space orbitals of $n\pi\pi_1^*\pi_2^*$. These orbitals are shown in Fig. S2. The second, third and fourth columns represent the coefficients of configuration interaction wavefunctions associated with the S_0, S_1 and S_2 states Corresponding to the transition between the active space orbitals. The numbers in bold font reveal strong mixing between the S_1-S_2 states

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$n\pi\pi_1^*\pi_2^*$	S_0	S_1	S_2
2200	0.9842357	-0.0032572	-0.0006302
2ba0	-0.0022846	**-0.5178297**	**-0.4236309**
2ab0	0.0022846	**0.5178297**	**0.4236309**
b2a0	0.0006726	**-0.4225931**	**0.5165817**
a2b0	-0.0006726	**0.4225931**	**-0.5165817**
20ab	-0.0001213	0.1767158	0.1445192
20ba	0.0001213	-0.1767158	-0.1445192
aabb	0.0032851	0.0997484	-0.1219347
bbaa	0.0032851	0.0997484	-0.1219347
2002	-0.1157341	-0.0016340	0.0040155
abab	-0.0036956	-0.0871044	0.1064116
baba	-0.0036956	-0.0871044	0.1064116
2020	-0.1026442	0.0072943	-0.0091700
b0a2	0.0003179	0.0640672	-0.0782505
a0b2	-0.0003179	-0.0640672	0.0782505
2b0a	0.0600289	0.0052125	-0.0062727
2a0b	-0.0600289	-0.0052125	0.0062727