Supporting Information

Reduction of CO_2 in the Presence of Light *via* Excited-state Hydride Transfer Reaction in a NADPH-inspired Derivative

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Contents

1. Computational details

The vertical transition energies from the ground to the low-lying excited states have been calculated at the equilibrium geometry of the ground electronic state of the **1d**···CO_2 complex, at the equilibrium geometry of the first excited state of the **1d**···CO_2 complex, and at the ground electronic state of the **2d**···HCO_2^- complex. The energies have been obtained employing the complete-active-space self-consistent-field (CASSCF)[1,2] method complemented by second-order multireference perturbation theory (CASPT2) using the internally contracted multi-reference second-order perturbation theory code (RS2C)[3] as implemented in the program system Molpro.[4] The active space for the CASSCF calculations consisted of 14 orbitals and 6 electrons. It comprised three doubly occupied π orbitals and eleven lowest unoccupied orbitals. All doubly occupied orbitals from the active space are located on the **1d** species. Among the unoccupied orbitals, two orbitals are located on the CO_2 molecule, two π* orbitals on the **1d** species and four σ* orbitals on the **1d** species while the remaining three unoccupied orbitals are diffuse and possess also charge distributions located between the H atom of the **1d** species and carbon of CO_2 (see Figure S1). The calculations were performed as state-averaged calculations and included first five singlet states and first three triplet states employing equal weights for all states. CASPT2 calculations were performed with a standard level shift of 0.3 au. For comparison, the calculations of the vertical excitation energies at the minimum of the ground state of **1d** were also performed at the CASSCF/CASPT2 level. The active space for the CASSCF calculations consisted of 12 active orbitals and 8 electrons (see Figure S2). The vertical spectrum of **1d** is presented in the main paper (Table 2). The orbitals for the active space employed for the calculations of the vertical spectrum of the ground state of the **2d**···HCO_2^- complex are given in Figure S3. The basis sets employed were segmented contracted def2-type basis sets. They consist of a def2-TZVP basis set on carbon and def2-SVP basis sets on oxygen, nitrogen and hydrogen. Additional numerous test calculations for the selection of orbitals for the active space were performed employing the abovementioned basis set. The five-membered ring of the benzimidazole unit does not retain planar geometry along the hydride-transfer reaction pathway and thus the separation between σ-π molecular orbitals is not conserved. Because of the mixing of orbitals of π origin with orbitals of σ origin and also valence-Rydberg mixing, it was not an easy task to select the set of orbitals for the active space. For example, the smaller active space (denoted 6-orbital active space in Table S1) involved two highest occupied molecular orbitals (HOMO) of π character and lowest unoccupied π* molecular orbitals (LUMO) and also two orbitals mainly located on the carbon atom of CO_2 (62a-67a) at the expense of eliminating other frontier orbitals. The CASPT2 vertical excitation energies, dipole moments and oscillator strengths calculated at the minimum of the ground state of the **1d**···CO_2 complex employing this smaller active space for the CASSCF calculations are presented in Table S1. The results for several other geometries on the reaction path for the hydride detachment indicate that inclusion of σ* orbitals for the description of low-lying and photochemically relevant πσ* excited states of the **1d**···CO_2 complex is needed.

The geometry optimization of the conical intersection between S_0 and S_1 was performed at the CASSCF level using the def2-SVP basis set for all atoms and the procedure implemented in Molpro program package. The active space consisted of 6 orbitals (orbitals 62a - 67a in Figure S1) and 4 electrons. The optimized geometry is presented in Figure S4. The geometry is characterized by the carbon atom of CO_2 at higher position than oxygen atoms with respect to the plane of the benzimidazoline unit while the geometry of the conical intersection obtained at the CASPT2 level (Figure 8 in the main paper) shows opposite characteristic: the carbon atom is at a lower position than the oxygens. The comparison of the CASPT2 energies of both geometries shows that the S_0/S_1 conical intersection presented in Figure 8 is at lower energy with respect to the ground state of the **1d**···CO_2 complex. Therefore, for further analysis we have adopted the CASPT2 geometry displayed in Figure 8.

The intrinsic reaction coordinate (IRC) calculations[5,6] for the first singlet excited state have been performed at the time dependent DFT (TD-DFT) level employing the analytic second derivatives and wB97XD functional.[7] The initial geometry was the geometry of the excited transition state (TS) for the reaction **1d**···CO_2 → **2d**···HCO_2^- and the reaction path was followed in both forward and reverse direction from that geometry. The IRC coordinate is a combination of the O-C-O bending, the C-H···C coordinate which involves changing the distance between the carbon of CO_2 and the hydrogen of the organo-hydride and out-of-plane distortion of the five-membered ring system of the benzimidazoline unit. The critical C···H distances and O-C-O angles for the hydride transfer reaction are given in Table S2. All DFT/TD-DFT calculations are performed with the Gaussian software package.[8]

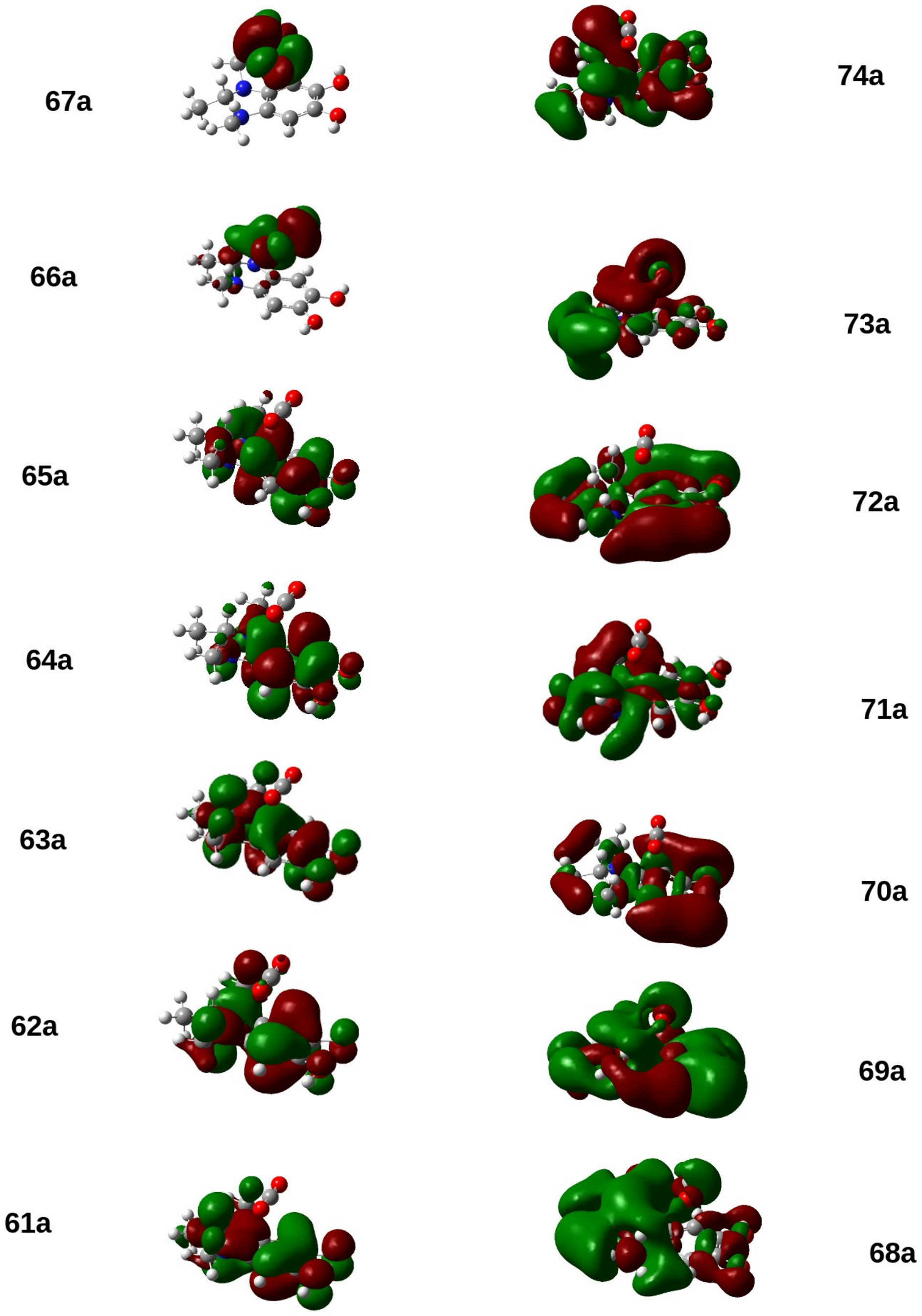

Figure S1

Molecular orbitals included in the active space of the CASSCF/CASPT2 calculations obtained at the optimized geometry of the electronic ground state of the **1d**···CO_2 complex.

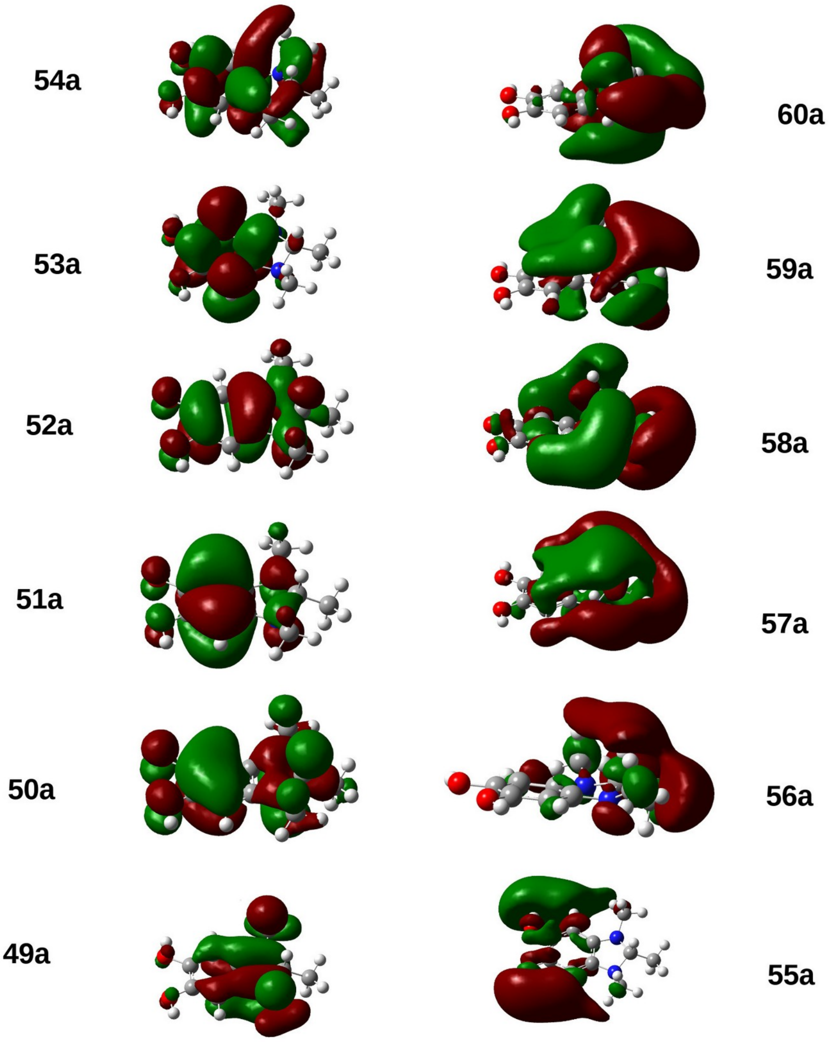

Figure S2

Molecular orbitals included in the active space of the CASSCF/CASPT2 calculations obtained at the optimized geometry of the electronic ground state of **1d**.

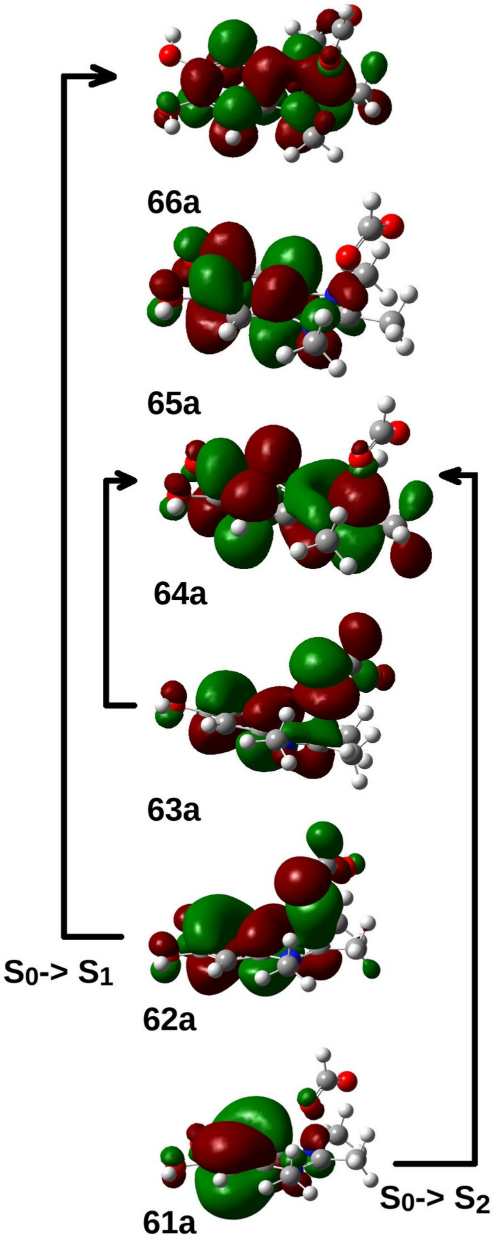

Figure S3

The frontier molecular orbitals involved in the electronic excitations of the lower-lying excited states of the **2d**···HCO_2^- complex obtained from CASSCF calculations and determined at the equilibrium geometry of the ground electronic state of the **2d**···HCO_2^- complex.

Table S1

Vertical excitation energies (ΔE), oscillator strengths (*f*), dipole moments (*μ*) for the lower-lying singlet and triplet electronic states of the **1d**···CO_2 complex calculated at the minimum of the ground electronic state employing the CASPT2 method and def2-TZVP basis set on carbon and def2-SVP basis set on O, N, and H. The results are related to the 6-orbital active space.

State	ΔE (eV)	*f*	*μ* (D)	Electronic excitation
1d•••CO_2 (S_0) 6-orbital active space				
S_0	0.00	-	3.56	
S_1 ($^1\pi\pi^*$)	3.59	0.1158	3.50	(63a → 64a) + (62a → 65a)
S_2 ($^1\pi\pi^*$)	5.08	0.037	3.62	(63a → 65a) + (62a → 64a)
S_3 ($^1\pi\sigma^*$)	5.48	0.010	6.98	(63a → 66a)
S_4 ($^1\pi\sigma^*$)	6.14	0.385	3.84	(62a → 65a)+(63a → 67a)
T_1 ($^3\pi\pi^*$)	3.20	-	3.20	(63a → 64a)
T_2 ($^3\pi\pi^*$)	3.39	-	2.92	(63a → 65a)
T_3 ($^3\pi\pi^*$)	4.60	-	3.73	(62a → 64a)

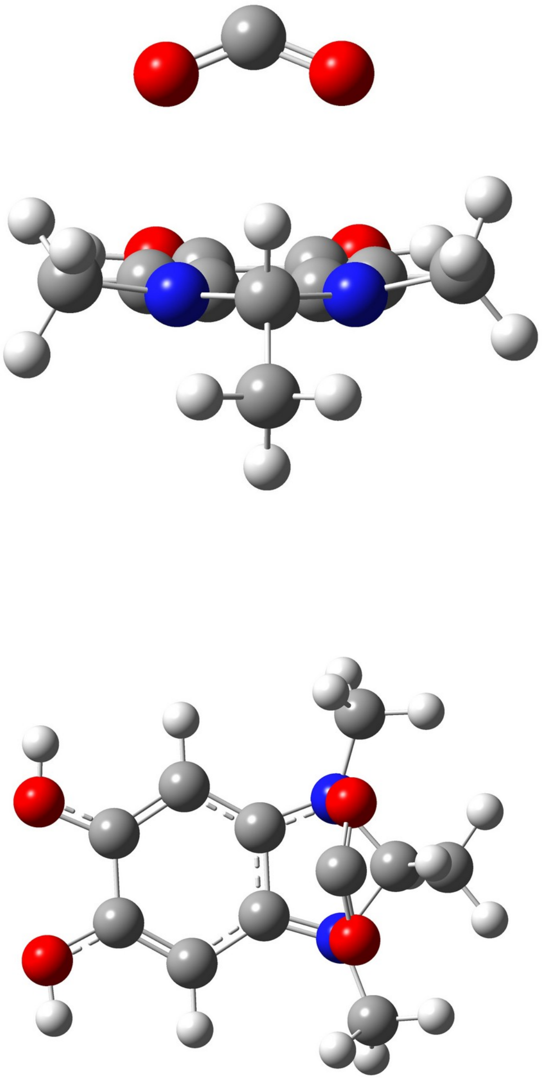

Figure S4

Geometry of the S_1/S_0 conical intersection of the **1d**···CO_2 complex obtained from the optimization at the CASCF level (side and top views).

Table S2

IRC reaction coordinates and critical C···H distances and O-C-O angles for the hydride transfer reaction in the **1d**···CO_2 complex calculated for the first singlet excited state.

IRC reaction coordinate	C···H [Å]	O-C-O [º]	IRC reaction coordinate	C···H [Å]	O-C-O [º]
0	1.298	137.8	1	1.110	133.6
-1	1.782	141.7	2	1.109	134.0
-2	2.067	144.3	3	1.129	137.3
-3	2.130	141.5	4	1.140	139.3
-4	2.199	139.5	5	1.146	140.0
-5	2.288	138.8	6	1.152	140.6
-6	2.391	138.0	7	1.159	141.4
-7	2.509	136.9	8	1.165	142.1
-8	2.599	135.6	9	1.169	142.7

5. References

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