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Supporting Information: Non-radiative decay of eumelanin monomer: To be or not to be planar

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S1 Optimized ground state of DHI at different methods

S1.1 Optimized ground state geometry at RI-MP2/cc-pVTZ level of theory

C	0.540472	1.481130	0.000000
C	-0.695363	0.799872	0.000000
C	-0.790071	-0.626245	0.000000
C	0.407715	-1.388059	0.000000
C	1.626219	-0.716606	0.000000
C	1.700837	0.710434	0.000000
C	-2.188766	-0.955182	0.000000
C	-2.884858	0.246198	0.000000
N	-1.983672	1.294820	0.000000
O	2.865077	-1.332712	0.000000
O	2.924128	1.324025	0.000000
H	-2.634745	-1.949920	0.000000
H	-3.958440	0.435696	0.000000
H	0.623508	2.572467	0.000000
H	0.380996	-2.484932	0.000000
H	-2.232519	2.276550	0.000000
H	3.576771	0.605228	0.000000
H	2.720836	-2.289647	0.000000

S1.2 Optimized ground state geometry at (12o,10e) SA-CASSCF/6-311++g(d,p) level of theory

C	0.5398418239	1.4590480814	0.0000000000
C	-0.6920240928	0.7894290274	0.0000000000
C	-0.7807795430	-0.6085472932	0.0000000000
C	0.4014282579	-1.3725481500	0.0000000000
C	1.6158778061	-0.7157485491	0.0000000000
C	1.6902638125	0.6929326031	0.0000000000

C	-2.1866842352	-0.9394361834	0.0000000000
C	-2.8654114749	0.2386513882	0.0000000000
N	-1.9711322823	1.2927062712	0.0000000000
O	2.8245860334	-1.3536267515	0.0000000000
O	2.8929696395	1.3084981618	0.0000000000
H	-2.6221156100	-1.9175963240	0.0000000000
H	-3.9203729094	0.4183904932	0.0000000000
H	0.6180610767	2.5306661922	0.0000000000
H	0.3669807643	-2.4489287539	0.0000000000
H	-2.2154709936	2.2518594524	0.0000000000
H	3.5815943911	0.6651962961	0.0000000000
H	2.7205125357	-2.2878289617	0.0000000000

S2 Vertical excitation energies (VEEs) in eV of DHI with (3o,2e) active space at 6-311++g(d,p) basis set

State	CASSCF (3o,2e)	CASPT2 (3o,2e)	EOM-EE-CCSD	Character
S_1	**5.51**	**5.67**	**4.55**	1π-$\pi^\star$
S_2	4.54	4.90	4.84	1π-$\sigma^\star$

S3 Histogram of dihedral angle of DHI at which surface hop occurs

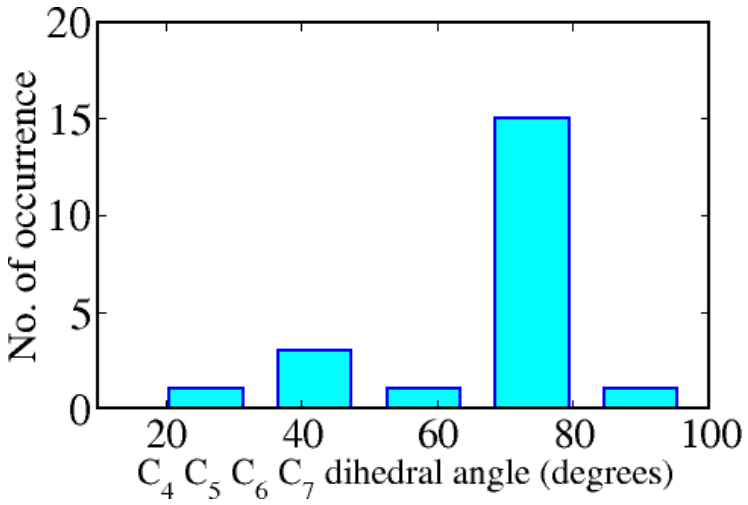
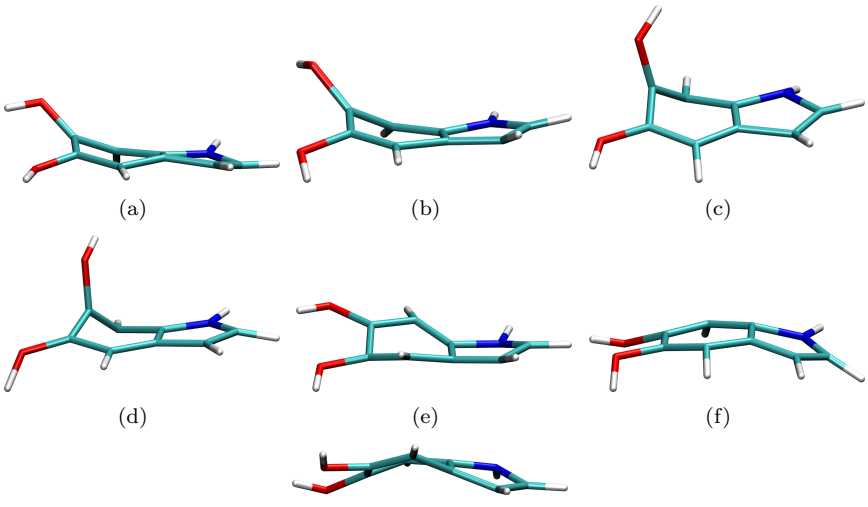


Figure S1: Histogram of C_4-C_5-C_6-C_7 dihedral angle at which surface hop occurs

S4 DHI at different trajectories



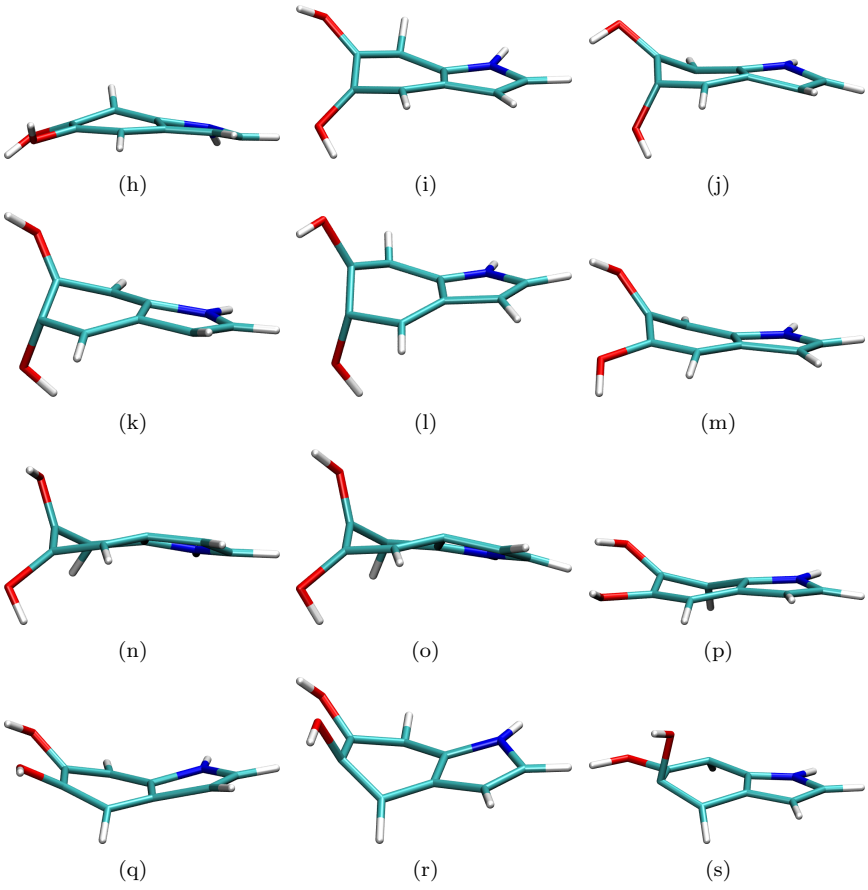


Figure S2: Different snapshots of DHI at different trajectory which proves that the molecule roams around in the nonplanar geometries at its excited state

S5 Excitation energies at the starting geometries obtained from Wigner distribution

Number of geometries	Excitation energy of S_1 (eV)	Excitation energy of S_2 (eV)
Geometry 1	3.69 ($\pi\sigma^\star$)	3.99($\pi\pi^\star$)
Geometry 2	4.18 ($\pi\sigma^\star$)	4.45 ($\pi\sigma^\star$)
Geometry 3	3.95 ($\pi\sigma^\star$)	4.30 ($\pi\sigma^\star$)
Geometry 4	3.89 ($\pi\pi^\star$)	4.06 ($\pi\pi^\star$)
Geometry 5	3.76 ($\pi\sigma^\star$)	3.89 ($\pi\pi^\star$)
Geometry 6	3.67 ($\pi\sigma^\star$)	4.04 ($\pi\pi^\star$)
Geometry 7	3.68 ($\pi\pi^\star$)	3.87 ($\pi\sigma^\star$)
Geometry 8	3.45 ($\pi\sigma^\star$)	3.65 ($\pi\pi^\star$)
Geometry 9	4.03 ($\pi\sigma^\star$)	4.21 ($\pi\pi^\star$)
Geometry 10	3.85 ($\pi\sigma^\star$)	4.01 ($\pi\pi^\star$)

Table S1: Excitation energies of starting geometries obtained from Wigner distribution to show that at these geometries S_1 and S_2 states are very close to each other

S6 Nature of excited state of a trajectory started from S_1

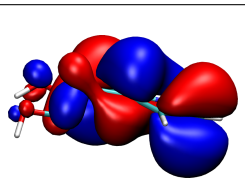
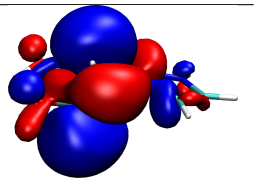
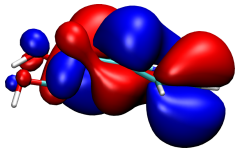
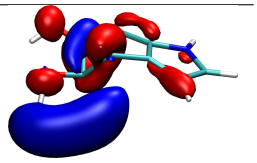
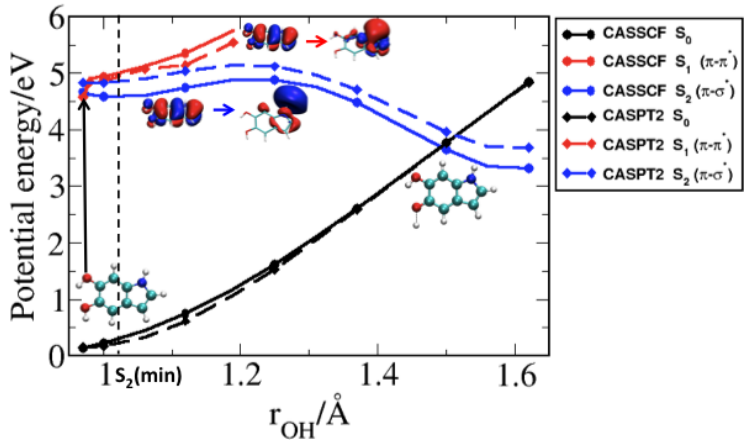
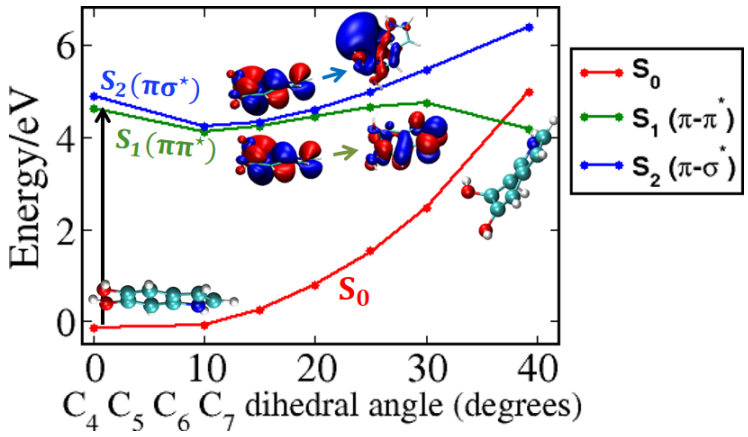
States	Nature	Initial orbital	Final orbital
S_1	$\pi\pi^\star$		
S_2	$\pi\sigma^\star$		

Table S2: Excited states at surface hopping geometry of DHI of a particular trajectory which started from S_1 state

S7 SA-CASSCF potential energy surface (PES) of DHI starting from FC to MECPs



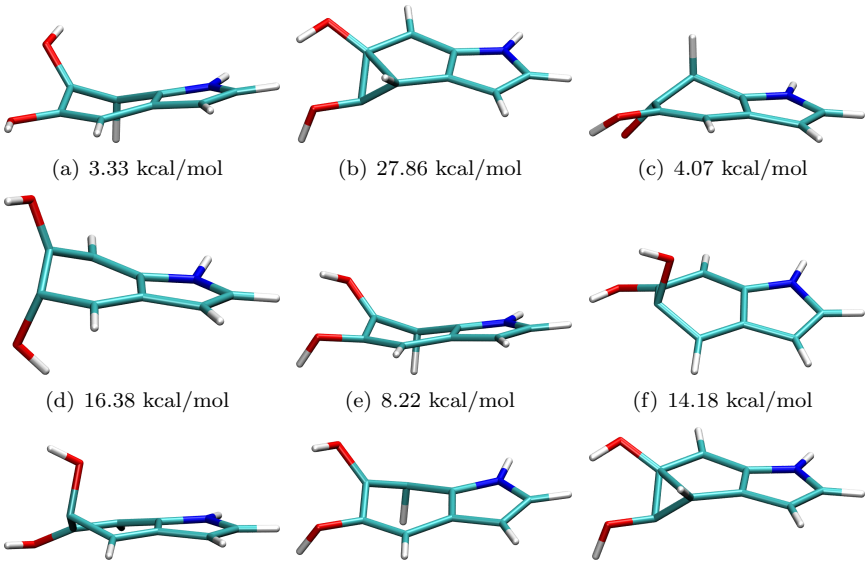
(a)



(b)

Figure S3: (a) SA-CASSCF PES of DHI starting from FC to planar S_0-S_2 ($\pi - \sigma^*$) MECP. (b) SA-CASSCF PES of DHI starting from FC to nonplanar S_0-S_1 ($\pi - \pi^*$) MECP

S8 Non planar MECPs of DHI with different C_4-C_5-C_6-C_7 dihedral angles



(a) 3.33 kcal/mol (b) 27.86 kcal/mol (c) 4.07 kcal/mol

(d) 16.38 kcal/mol (e) 8.22 kcal/mol (f) 14.18 kcal/mol

(g) 14.19 kcal/mol (h) 8.28 kcal/mol (i) 27.86 kcal/mol

Figure S4: Non planar MECPs of DHI

S9 Topological parameters around the surface of nonplanar MECP of DHI

$$\begin{aligned} \sigma_x &= 0.00562 \\ \sigma_y &= 0.44572 \\ d_{gh} &= 0.16662 \\ \Delta_{gh} &= 0.61658 \end{aligned}$$

S9.1 g and h vectors around the surface of nonplanar MECP of DHI

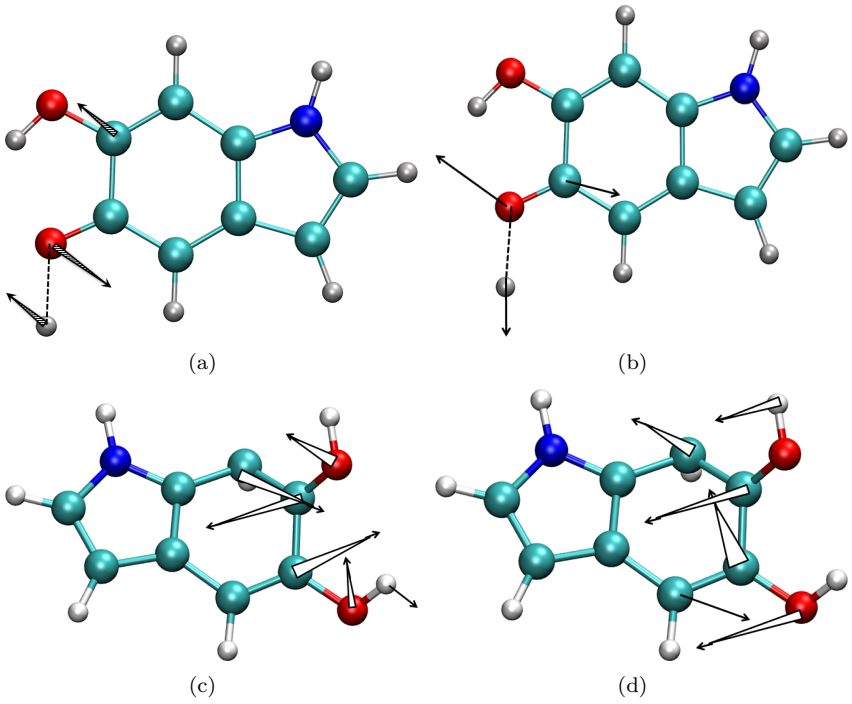
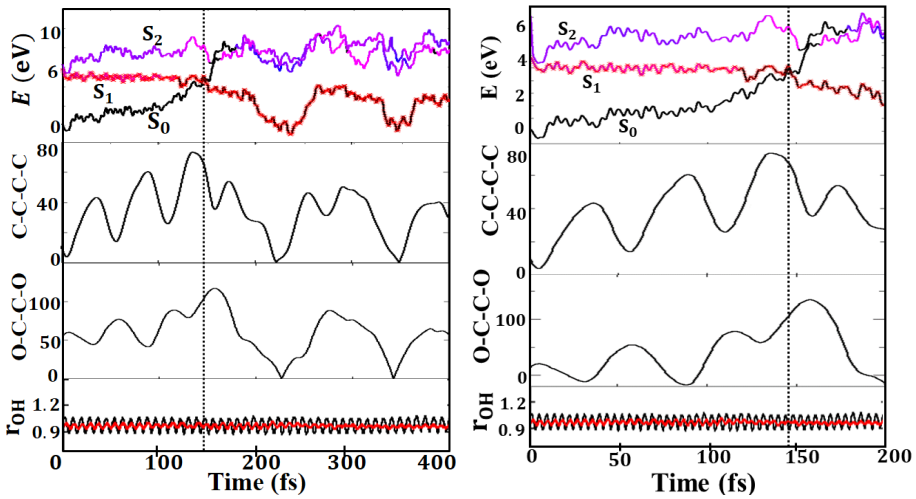


Figure S5: (a) g-vector around S_0-S_2 CI along r_{O_5H} elongation of DHI. (b) h-vector around S_0-S_2 CI along r_{O_5H} elongation of DHI. (c) g-vector around S_0-S_1 nonplanar CI of DHI. (d) (a) h-vector around S_0-S_1 nonplanar CI of DHI.

S10 Comparison of result of dynamics with (3o,2e)/6-31g and (12o,10e)/6-311++g(d,p) level of theory



(a) (b)

Figure S6: A representative of type II trajectory which deactivates at 146.5 fs (3o,2e/6-31g) and at 146 fs (12o,10e/6-311++g(d,p)) through $S_1 \rightarrow S_0$ pathway: (a) with (3o,2e)/6-31g level of theory. (b) with (12o,10e)/6-311++g(d,p) level of theory. The energy of the two lowest lying excited and ground states are shown along the trajectories. The red symbol denotes the occupation of the state by the DHI molecule.

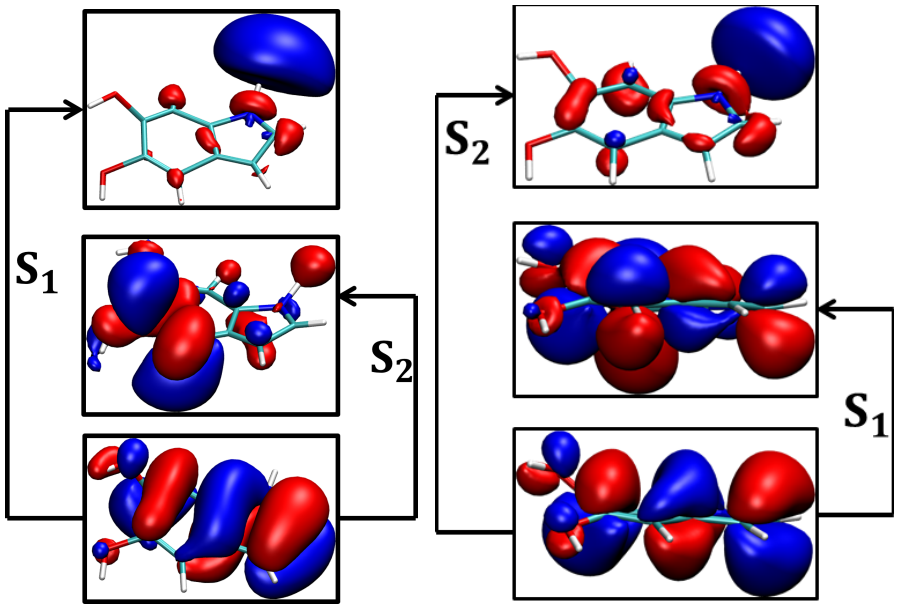


Figure S7: (a) States involved in a particular trajectory which deactivates from S_1 to S_0 at (3o,2e)/6-31g level of theory. (b) States involved of that particular trajectory at (12o,10e)/6-311++g(d,p) level of theory