Supporting Information for

Four resonance structures elucidate double-bond isomerization of a biological chromophore

Evgeniy V. Gromov and Tatiana Domratcheva

Department of Biomolecular Mechanisms, Max-Planck Institute for Medical Research

Jahnstraße 29, D-69120 Heidelberg, Germany

evgeniy.gromov@mpimf-heidelberg.mpg.de tatjana.domratcheva@mpimf-heidelberg.mpg.de

Contents

Page

Table S.1: Relative S_0 and S_1 energies (eV) and differences in the permanent dipole moments of the S_1 and S_0 states ($\Delta\mu = \vec{\mu}_{S_1} - \vec{\mu}_{S_0}$, in Debye) at the different stationary points and points of S_1/S_0 minimum energy conical intersections for models **1**, **2** and **3**. In parentheses, $S_0 \rightarrow S_1$ oscillator strengths.

Point	**1**			**2**			**3**		
	S_0	S_1	$\Delta\mu$	S_0	S_1	$\Delta\mu$	S_0	S_1	$\Delta\mu$
E-S_0	0.00	2.60 (1.008)	4.1	0.00	2.49 (1.063)	2.1	0.00	2.74 (0.900)	8.5
E-S_1-Sad/Min	0.08	2.52 (0.953)	4.8	0.12	2.39 (0.983)	3.2	0.09	2.65 (0.900)	7.6
α-S_1-Min/Sad	0.96	2.39 (<0.001)	19.0	1.20	2.14 (<0.001)	19.8	0.81	2.81 (<0.001)	19.1
α-CoIn	2.85	2.87 (<0.001)	17.1	2.53	2.56 (<0.001)	17.8	3.51	3.54 (<0.001)	12.9
β-S_1-Sad	0.75	2.69 (0.626)	2.0	0.88	2.72 (0.534)	4.8	0.81	2.79 (0.669)	2.3
β-S_1-Min	1.65	2.43 (<0.001)	14.7	1.58	2.56 (<0.001)	14.7	2.05	2.34 (<0.001)	15.4
β-CoIn	2.63	2.65 (<0.001)	14.8	2.82	2.84 (<0.001)	14.5	2.38	2.40 (<0.001)	15.2
Z-S_0	0.20	2.72 (0.799)	2.4	0.26	2.71 (0.792)	1.5	0.22	2.84 (0.751)	6.7

Table S.2: Total XMCQDPT2 S_0 and S_1 energies (hartree) at the different stationary points and points of S_1/S_0 minimum energy conical intersections for models **1**, **2** and **3**.

Point	**1**		**2**		**3**	
	S_0	S_1	S_0	S_1	S_0	S_1
E-S_0	-933.094991	-932.999397	-1009.346109	-1009.254484	-1085.607672	-1085.507005
E-S_1-Sad/Min	-933.091942	-933.002256	-1009.341878	-1009.258277	-1085.604470	-1085.510296
α-S_1-Min/Sad	-933.059755	-933.007213	-1009.302047	-1009.267585	-1085.577890	-1085.504463
α-CoIn	-932.990230	-932.989361	-1009.253066	-1009.252228	-1085.478626	-1085.477683
β-S_1-Sad	-933.067416	-932.996082	-1009.313808	-1009.246068	-1085.578050	-1085.505322
β-S_1-Min	-933.034234	-933.005559	-1009.288018	-1009.251880	-1085.532401	-1085.521689
β-CoIn	-932.998358	-932.997556	-1009.242359	-1009.241615	-1085.520251	-1085.519560
Z-S_0	-933.087711	-932.995084	-1009.336740	-1009.246605	-1085.599486	-1085.503441

Table S.3: Basis set superposition error (BSSE) corrections to the S_0 and S_1 total and relative (in parentheses) energies (eV) at the different stationary points for models **2** and **3**.

Point	**2**		**3**	
	S_0	S_1	S_0	S_1
E-S_0	0.098 (0.000)	0.119 (0.021)	0.323 (0.000)	0.328 (0.004)
E-S_1-Sad/Min	0.119 (0.021)	0.142 (0.044)	0.306 (-0.017)	0.315 (-0.008)
α-S_1-Min/Sad	0.129 (0.031)	0.169 (0.071)	0.312 (-0.012)	0.239 (-0.085)
β-S_1-Sad	0.101 (0.003)	0.104 (0.006)	0.287 (-0.036)	0.310 (-0.018)
β-S_1-Min	0.101 (0.003)	0.074 (-0.024)	0.281 (-0.042)	0.336 (0.013)

Table S.4: Selected bonds lengths (Å), and α and β torsional (dihedral) angles (°) at the different stationary points for models **1** (first number), **2** (second number) and **3** (third number). For the atom numbers and definition of α and β see Figure 1b of the paper.

	E-S_0	E-S_1-Sad/Min	α-S_1-Min/Sad	α-CoIn
O_1-C_1	1.259/1.256/1.292	1.271/1.270/1.296	1.266/1.265/1.281	1.264/1.262/1.281
C_1-C_2	1.472/1.474/1.455	1.462/1.463/1.452	1.461/1.462/1.456	1.457/1.460/1.453
C_2-C_3	1.384/1.382/1.391	1.401/1.400/1.399	1.393/1.393/1.393	1.386/1.387/1.386
C_3-C_4	1.440/1.443/1.432	1.440/1.436/1.445	1.437/1.435/1.437	1.444/1.441/1.461
C_4-C_5	1.438/1.442/1.429	1.436/1.432/1.441	1.437/1.435/1.437	1.452/1.448/1.458
C_5-C_6	1.388/1.384/1.395	1.399/1.400/1.395	1.392/1.393/1.393	1.380/1.382/1.379
C_6-C_1	1.466/1.467/1.448	1.465/1.464/1.457	1.461/1.462/1.456	1.461/1.462/1.463
C_4-C_7	1.428/1.421/1.443	1.466/1.473/1.450	1.485/1.488/1.483	1.490/1.494/1.460
C_7-C_8	1.392/1.398/1.381	1.408/1.398/1.415	1.416/1.401/1.417	1.494/1.459/1.503
C_8-C_9	1.447/1.440/1.459	1.443/1.452/1.439	1.420/1.429/1.421	1.400/1.399/1.419
C_9-O_2	1.236/1.251/1.232	1.254/1.269/1.252	1.256/1.280/1.255	1.252/1.291/1.249
C_9-S	1.858/1.847/1.841	1.872/1.850/1.871	1.906/1.867/1.899	1.981/1.904/1.906
S-C_{10}	1.816/1.821/1.817	1.816/1.824/1.816	1.815/1.825/1.815	1.813/1.821/1.815
$O_1 \cdots H$	1.778	1.837	1.929	1.934
$O_1 \cdots H$	1.776	1.839	1.931	1.951
$O_2 \cdots H$	1.901	1.833	1.769	1.699
α	180.0/179.8/179.9	180.0/-179.8/-179.9	89.1 / 89.2/90.0	-77.2/-70.4/-85.2
β	180.0/179.9/179.9	180.0/ 178.9/-179.9	-178.5/-178.5/179.6	137.1/145.4/-122.1

Table S.4: Continuation

	β-S_1-Sad	β-S_1-Min	β-CoIn	Z-S_0
O_1-C_1	1.264/1.265/1.288	1.271/1.271/1.301	1.277/1.276/1.311	1.258/1.257/1.290
C_1-C_2	1.467/1.467/1.457	1.462/1.462/1.450	1.457/1.457/1.445	1.469/1.470/1.453
C_2-C_3	1.392/1.391/1.391	1.393/1.393/1.394	1.400/1.399/1.399	1.384/1.383/1.391
C_3-C_4	1.452/1.451/1.454	1.447/1.447/1.447	1.441/1.441/1.445	1.446/1.448/1.436
C_4-C_5	1.448/1.448/1.450	1.444/1.444/1.445	1.439/1.439/1.441	1.445/1.448/1.436
C_5-C_6	1.389/1.390/1.389	1.393/1.393/1.394	1.399/1.398/1.399	1.384/1.383/1.391
C_6-C_1	1.471/1.469/1.461	1.462/1.462/1.449	1.458/1.458/1.444	1.468/1.469/1.450
C_4-C_7	1.424/1.423/1.416	1.421/1.421/1.416	1.447/1.443/1.424	1.425/1.421/1.441
C_7-C_8	1.471/1.472/1.473	1.470/1.470/1.472	1.471/1.473/1.470	1.406/1.412/1.394
C_8-C_9	1.482/1.436/1.427	1.460/1.461/1.462	1.496/1.498/1.483	1.443/1.435/1.456
C_9-O_2	1.245/1.254/1.247	1.234/1.228/1.229	1.217/1.223/1.221	1.237/1.247/1.232
C_9-S	1.886/1.851/1.885	1.834/1.848/1.839	1.822/1.808/1.827	1.874/1.857/1.854
S-C_{10}	1.816/1.820/1.816	1.820/1.818/1.818	1.820/1.823/1.819	1.816/1.818/1.816
$O_1 \cdots H$	1.827	1.762	1.721	1.790
$O_1 \cdots H$	1.829	1.760	1.719	1.783
$O_2 \cdots H$	1.872	1.967	2.033	1.929
α	-173.0/-171.8/-176.2	176.6/ 177.5/177.7	158.8/161.5/174.6	180.0/179.7/-179.7
β	128.9/ 122.7/ 133.8	91.6/ 90.1/ 90.6	102.5/101.2/ 88.4	0.6/ 0.8/ 0.1

Table S.5: Net atomic charges (charges at the adjacent hydrogens are included) in the S_0 and S_1 states at the different stationary points for models **1** (first number), **2** (second number) and **3** (third number). For the atom numbers see Figure 1b of the paper.

	E-S_0		E-S_1-Sad/Min	
	S_0	S_1	S_0	S_1
O_1	-0.44/-0.42/-0.61	-0.42/-0.42/-0.51	-0.46/-0.42/-0.59	-0.42/-0.42/-0.51
C_1	0.19/ 0.19/ 0.22	0.16/ 0.16/ 0.21	0.19/ 0.19/ 0.21	0.16/ 0.16/ 0.20
C_2	-0.10/-0.09/-0.09	-0.07/-0.07/-0.03	-0.09/-0.09/-0.08	-0.07/-0.07/-0.04
C_3	0.00/ 0.01/ 0.00	-0.04/-0.04/-0.01	-0.00/ 0.01/ 0.01	-0.03/-0.04/-0.01
C_4	-0.22/-0.21/-0.21	-0.06/-0.07/-0.05	-0.22/-0.21/-0.21	-0.06/-0.07/-0.06
C_5	0.02/ 0.03/ 0.02	-0.01/-0.01/ 0.01	0.02/ 0.03/ 0.02	-0.01/-0.01/ 0.01
C_6	-0.13/-0.12/-0.11	-0.05/-0.05/-0.01	-0.12/-0.12/-0.10	-0.04/-0.05/-0.01
C_7	0.15/ 0.16/ 0.17	0.04/ 0.05/ 0.03	0.14/ 0.16/ 0.15	0.02/ 0.05/ 0.03
C_8	-0.19/-0.19/-0.14	-0.14/-0.09/-0.19	-0.16/-0.19/-0.12	-0.13/-0.09/-0.16
C_9	0.19/ 0.18/ 0.19	0.10/ 0.09/ 0.10	0.18/ 0.18/ 0.19	0.10/ 0.09/ 0.10
O_2	-0.37/-0.43/-0.34	-0.41/-0.46/-0.41	-0.38/-0.43/-0.36	-0.43/-0.46/-0.43
S	-0.14/-0.13/-0.12	-0.14/-0.13/-0.13	-0.13/-0.13/-0.13	-0.14/-0.13/-0.13
C_{10}	0.04/ 0.03/ 0.05	0.04/ 0.03/ 0.05	0.04/ 0.03/ 0.05	0.04/ 0.03/ 0.04

Table S.5: Continuation

	α-S_1-Min/Sad		β-S_1-Min	
	S_0	S_1	S_0	S_1
O_1	-0.52/-0.51/-0.62	-0.32/-0.32/-0.41	-0.36/-0.36/-0.49	-0.47/-0.47/-0.62
C_1	0.16/ 0.16/ 0.17	0.17/ 0.17/ 0.21	0.22/ 0.21/ 0.27	0.14/ 0.14/ 0.17
C_2	-0.15/-0.14/-0.13	-0.01/-0.01/-0.00	-0.05/-0.05/-0.04	-0.10/-0.10/-0.08
C_3	-0.01/-0.01/ 0.00	0.04/ 0.04/ 0.06	0.10/ 0.09/ 0.12	-0.03/-0.04/-0.02
C_4	-0.34/-0.34/-0.32	0.02/ 0.02/ 0.03	-0.13/-0.13/-0.14	-0.16/-0.16/-0.15
C_5	-0.01/-0.01/ 0.00	0.04/ 0.04/ 0.06	0.05/ 0.05/ 0.07	-0.04/-0.03/-0.02
C_6	-0.15/-0.15/-0.13	-0.01/-0.01/ 0.00	-0.05/-0.05/-0.04	-0.11/-0.11/-0.09
C_7	0.21/ 0.23/ 0.21	-0.21/-0.17/-0.21	0.25/ 0.25/ 0.28	-0.14/-0.14/-0.08
C_8	0.02/ 0.02/ 0.03	-0.19/-0.14/-0.19	-0.55/-0.52/-0.54	0.11/ 0.12/ 0.12
C_9	0.22/ 0.23/ 0.22	0.06/ 0.03/ 0.07	0.12/ 0.13/ 0.12	0.19/ 0.22/ 0.19
O_2	-0.32/-0.36/-0.32	-0.47/-0.53/-0.46	-0.46/-0.51/-0.46	-0.27/-0.32/-0.27
S	-0.15/-0.13/-0.14	-0.16/-0.15/-0.16	-0.16/-0.14/-0.15	-0.15/-0.12/-0.13
C_{10}	0.03/ 0.04/ 0.04	0.03/ 0.03/ 0.04	0.03/ 0.02/ 0.04	0.04/ 0.02/ 0.04

Table S.5: Continuation

	Z-S_0	
	S_0	S_1
O_1	-0.43/-0.42/-0.59	-0.42/-0.42/-0.51
C_1	0.20/ 0.20/ 0.22	0.16/ 0.16/ 0.21
C_2	-0.11/-0.10/-0.10	-0.08/-0.07/-0.04
C_3	0.06/ 0.06/ 0.05	0.02/ 0.02/ 0.04
C_4	-0.27/-0.25/-0.26	-0.12/-0.14/-0.10
C_5	0.02/ 0.02/ 0.02	-0.02/-0.01/ 0.00
C_6	-0.13/-0.12/-0.12	-0.07/-0.07/-0.03
C_7	0.13/ 0.13/ 0.15	0.03/ 0.04/ 0.01
C_8	-0.16/-0.16/-0.11	-0.04/-0.01/-0.09
C_9	0.18/ 0.19/ 0.19	0.07/ 0.08/ 0.06
O_2	-0.36/-0.44/-0.33	-0.41/-0.48/-0.42
S	-0.15/-0.13/-0.13	-0.16/-0.14/-0.14
C_{10}	0.03/ 0.02/ 0.05	0.03/ 0.02/ 0.04

Table S.6: S_0 and S_1 charge distributions at the different stationary points in terms of the net charges on the phenolic (first number) and carbonyl (second number) moieties of the chromophore for models **1**, **2** and **3**. The charge on the water molecule(s) is not included.

	1		**2**		**3**	
	S_0	S_1	S_0	S_1	S_0	S_1
E-S_0	-0.69/-0.31	-0.48/-0.52	-0.61/-0.39	-0.50/-0.50	-0.77/-0.18	-0.40/-0.56
E-S_1-Sad/Min	-0.69/-0.31	-0.46/-0.54	-0.63/-0.36	-0.47/-0.52	-0.75/-0.22	-0.41/-0.55
α-S_1-Min/Sad	-1.01/0.01	-0.07/-0.93	-1.00/0.02	-0.05/-0.93	-1.01/0.04	-0.06/-0.91
β-S_1-Sad	-0.41/-0.59	-0.57/-0.43	-0.31/-0.69	-0.62/-0.38	-0.49/-0.48	-0.46/-0.51
β-S_1-Min	0.01/-1.01	-0.92/-0.08	0.02/-1.02	-0.91/-0.09	0.03/-0.99	-0.91/-0.05
Z-S_0	-0.67/-0.33	-0.52/-0.48	-0.61/-0.39	-0.52/-0.49	-0.77/-0.19	-0.43/-0.53

Table S.7: Number of unpaired electrons at the chromophore atoms in the S_0 and S_1 states at the different stationary points for models **1** (first number) **2** (second number) and **3** (third number). For the atom numbers see Figure 1b of the paper.

	E-S_0		E-S_1-Sad/Min	
	S_0	S_1	S_0	S_1
O_1	0.138/0.145/0.090	0.257/0.243/0.261	0.142/0.151/0.098	0.277/0.268/0.254
C_1	0.101/0.105/0.082	0.170/0.162/0.197	0.102/0.106/0.085	0.167/0.158/0.187
C_2	0.127/0.131/0.120	0.260/0.248/0.276	0.130/0.136/0.121	0.259/0.250/0.262
C_3	0.126/0.130/0.126	0.285/0.265/0.307	0.130/0.134/0.129	0.284/0.253/0.311
C_4	0.087/0.088/0.095	0.398/0.387/0.395	0.091/0.094/0.097	0.379/0.353/0.400
C_5	0.124/0.126/0.123	0.258/0.251/0.267	0.127/0.130/0.126	0.243/0.233/0.257
C_6	0.124/0.127/0.117	0.318/0.297/0.325	0.128/0.132/0.121	0.325/0.305/0.317
C_7	0.105/0.106/0.113	0.558/0.562/0.518	0.115/0.116/0.121	0.580/0.552/0.566
C_8	0.091/0.084/0.109	0.321/0.354/0.288	0.097/0.091/0.112	0.304/0.318/0.300
C_9	0.094/0.083/0.101	0.181/0.208/0.169	0.100/0.091/0.104	0.180/0.222/0.167
O_2	0.118/0.095/0.128	0.180/0.171/0.175	0.126/0.102/0.134	0.185/0.177/0.182
C_{10}	0.000/0.000/0.000	0.000/0.001/0.000	0.000/0.001/0.000	0.000/0.002/0.000
S	0.005/0.005/0.005	0.016/0.020/0.016	0.005/0.005/0.005	0.015/0.018/0.015

Table S.7: Continuation.

	α-S_1-Min/Sad		α-CoIn	
	S_0	S_1	S_0	S_1
O_1	0.117/0.118/0.090	0.379/0.383/0.331	0.120/0.118/0.099	0.375/0.375/0.326
C_1	0.087/0.088/0.074	0.165/0.165/0.164	0.088/0.088/0.091	0.164/0.163/0.190
C_2	0.115/0.115/0.111	0.306/0.309/0.289	0.119/0.114/0.122	0.270/0.318/0.241
C_3	0.114/0.114/0.117	0.186/0.185/0.184	0.121/0.112/0.139	0.183/0.178/0.178
C_4	0.098/0.098/0.107	0.402/0.399/0.411	0.108/0.102/0.151	0.398/0.411/0.330
C_5	0.115/0.114/0.117	0.186/0.186/0.184	0.114/0.117/0.146	0.174/0.185/0.196
C_6	0.115/0.115/0.111	0.305/0.308/0.290	0.114/0.116/0.125	0.315/0.283/0.251
C_7	0.170/0.159/0.174	0.586/0.569/0.576	0.406/0.316/0.554	0.674/0.696/0.552
C_8	0.142/0.130/0.147	0.188/0.161/0.198	0.325/0.233/0.481	0.204/0.155/0.334
C_9	0.120/0.124/0.121	0.188/0.228/0.185	0.140/0.146/0.156	0.137/0.158/0.155
O_2	0.156/0.157/0.158	0.190/0.200/0.191	0.201/0.208/0.221	0.162/0.172/0.202
C_{10}	0.000/0.001/0.000	0.000/0.004/0.000	0.001/0.002/0.002	0.001/0.003/0.002
S	0.005/0.004/0.006	0.016/0.015/0.016	0.008/0.004/0.014	0.011/0.007/0.015

Table S.7: Continuation.

	β-S_1-Sad		β-S_1-Min	
	S_0	S_1	S_0	S_1
O_1	0.164/0.174/0.113	0.213/0.212/0.182	0.208/0.210/0.156	0.236/0.239/0.163
C_1	0.112/0.117/0.089	0.141/0.140/0.145	0.135/0.136/0.107	0.145/0.146/0.147
C_2	0.142/0.149/0.125	0.195/0.190/0.191	0.173/0.174/0.152	0.180/0.183/0.151
C_3	0.139/0.144/0.131	0.223/0.210/0.241	0.164/0.165/0.149	0.183/0.182/0.202
C_4	0.102/0.110/0.098	0.294/0.267/0.307	0.152/0.153/0.137	/0.1670.168/0.160
C_5	0.137/0.142/0.130	0.211/0.203/0.225	0.165/0.166/0.151	0.182/0.181/0.202
C_6	0.141/0.148/0.126	0.225/0.209/0.229	0.178/0.180/0.158	0.171/0.173/0.148
C_7	0.146/0.158/0.143	0.638/0.620/0.600	0.239/0.242/0.209	0.490/0.484/0.555
C_8	0.095/0.081/0.120	0.489/0.541/0.412	0.037/0.038/0.035	0.787/0.781/0.792
C_9	0.085/0.075/0.092	0.152/0.160/0.138	0.059/0.053/0.060	0.155/0.153/0.154
O_2	0.113/0.099/0.126	0.204/0.209/0.189	0.086/0.078/0.087	0.253/0.238/0.253
C_{10}	0.000/0.000/0.000	0.001/0.001/0.001	0.000/0.000/0.000	0.000/0.001/0.000
S	0.004/0.004/0.005	0.015/0.018/0.013	0.003/0.003/0.003	0.018/0.021/0.018

Table S.7: Continuation.

	β-CoIn		Z-S_0	
	S_0	S_1	S_0	S_1
O_1	0.228/0.224/0.155	0.231/0.236/0.155	0.143/0.148/0.095	0.249/0.242/0.253
C_1	0.140/0.139/0.106	0.139/0.141/0.143	0.103/0.106/0.082	0.160/0.154/0.185
C_2	0.186/0.183/0.152	0.181/0.183/0.149	0.129/0.133/0.119	0.256/0.247/0.271
C_3	0.170/0.168/0.149	0.176/0.177/0.202	0.128/0.131/0.124	0.257/0.243/0.282
C_4	0.186/0.177/0.138	0.176/0.176/0.161	0.088/0.091/0.092	0.379/0.363/0.394
C_5	0.170/0.169/0.151	0.175/0.176/0.202	0.126/0.129/0.123	0.243/0.233/0.259
C_6	0.193/0.190/0.158	0.171/0.173/0.146	0.127/0.131/0.117	0.291/0.277/0.308
C_7	0.316/0.298/0.213	0.542/0.527/0.578	0.110/0.114/0.113	0.545/0.542/0.520
C_8	0.028/0.020/0.032	0.823/0.840/0.818	0.090/0.089/0.106	0.357/0.389/0.308
C_9	0.067/0.069/0.063	0.146/0.139/0.149	0.094/0.081/0.103	0.213/0.244/0.194
O_2	0.095/0.096/0.090	0.197/0.166/0.224	0.111/0.082/0.125	0.193/0.174/0.190
C_{10}	0.000/0.000/0.000	0.003/0.004/0.001	0.000/0.000/0.000	0.001/0.001/0.001
S	0.003/0.003/0.003	0.019/0.022/0.019	0.005/0.005/0.005	0.018/0.022/0.018

Table S.8: Total number of unpaired electrons in the S_0 and S_1 states and their difference (S_1–S_0) at the different stationary points for models **1** (first number) **2** (second number) and **3** (third number).

	α-S_1-Min/Sad	S_1-Min/Sad	S_0-Min	β-S_1-Sad	β-S_1-Min
S_0	1.4/1.3/1.3	1.3/1.3/1.3	1.2/1.2/1.2/	1.4/1.4/1.3	1.6/1.6/1.4
S_1	3.1/3.1/3.0	3.2/3.1/3.2	3.2/3.2/3.2/	3.0/3.0/2.9	3.0/3.0/3.0
S_1–S_0	1.8/1.8/1.7	1.9/1.8/2.0	2.0/2.0/2.0/	1.6/1.6/1.6	1.4/1.4/1.6

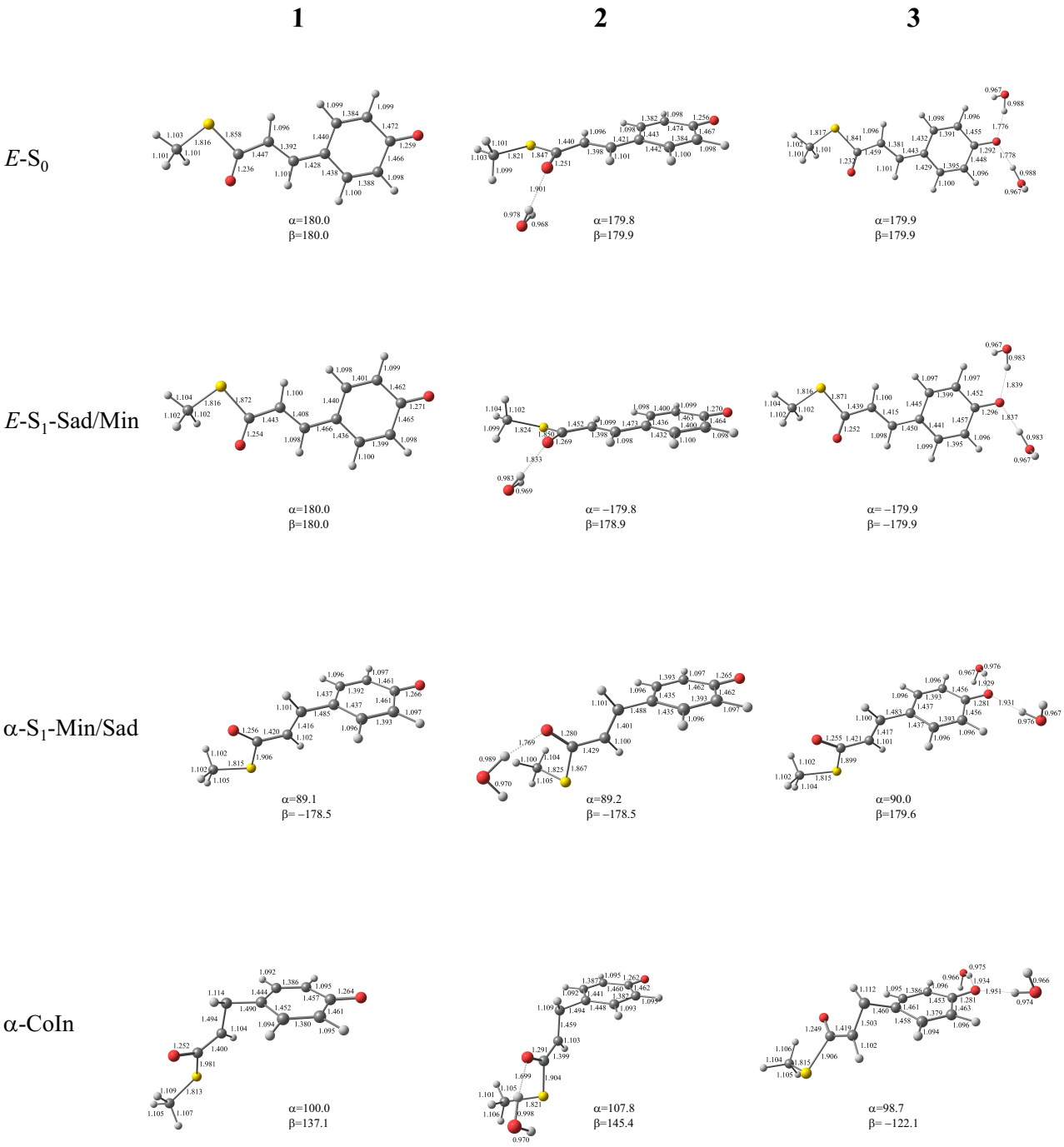


Figure S.1: Geometries of models **1-3** at the different stationary points and CoIns.

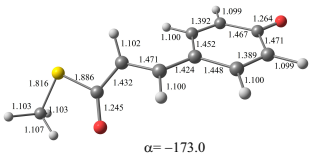
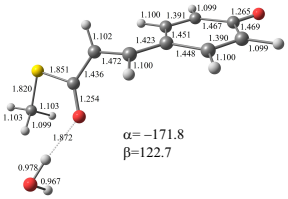
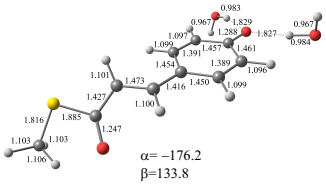
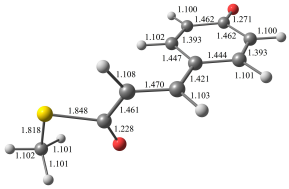
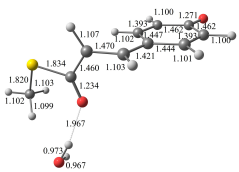
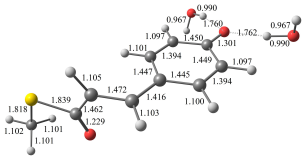
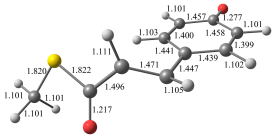
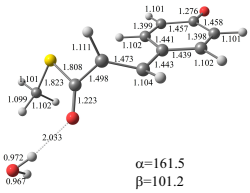
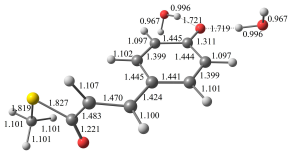
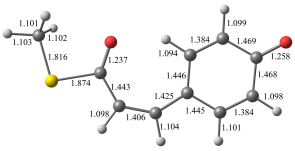
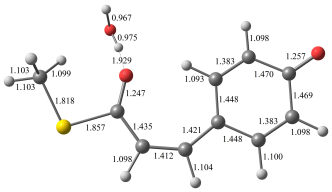
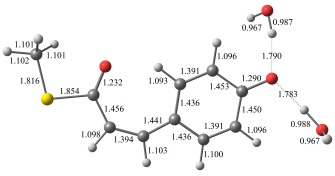
	1	2	3
β-S_1-Sad	 α= −173.0 β=128.0	 α= −171.8 β=122.7	 α= −176.2 β=133.8
β-S_1-Min	 α=176.6 β=91.6	 α=177.5 β=90.1	 α=177.7 β=90.6
β-CoIn	 α=158.8 β=102.5	 α=161.5 β=101.2	 α=174.6 β=88.4
Z-S_0	 α=180.0 β=0.6	 α=179.7 β=0.8	 α= −179.7 β=0.1

Figure S.1: Continuation.

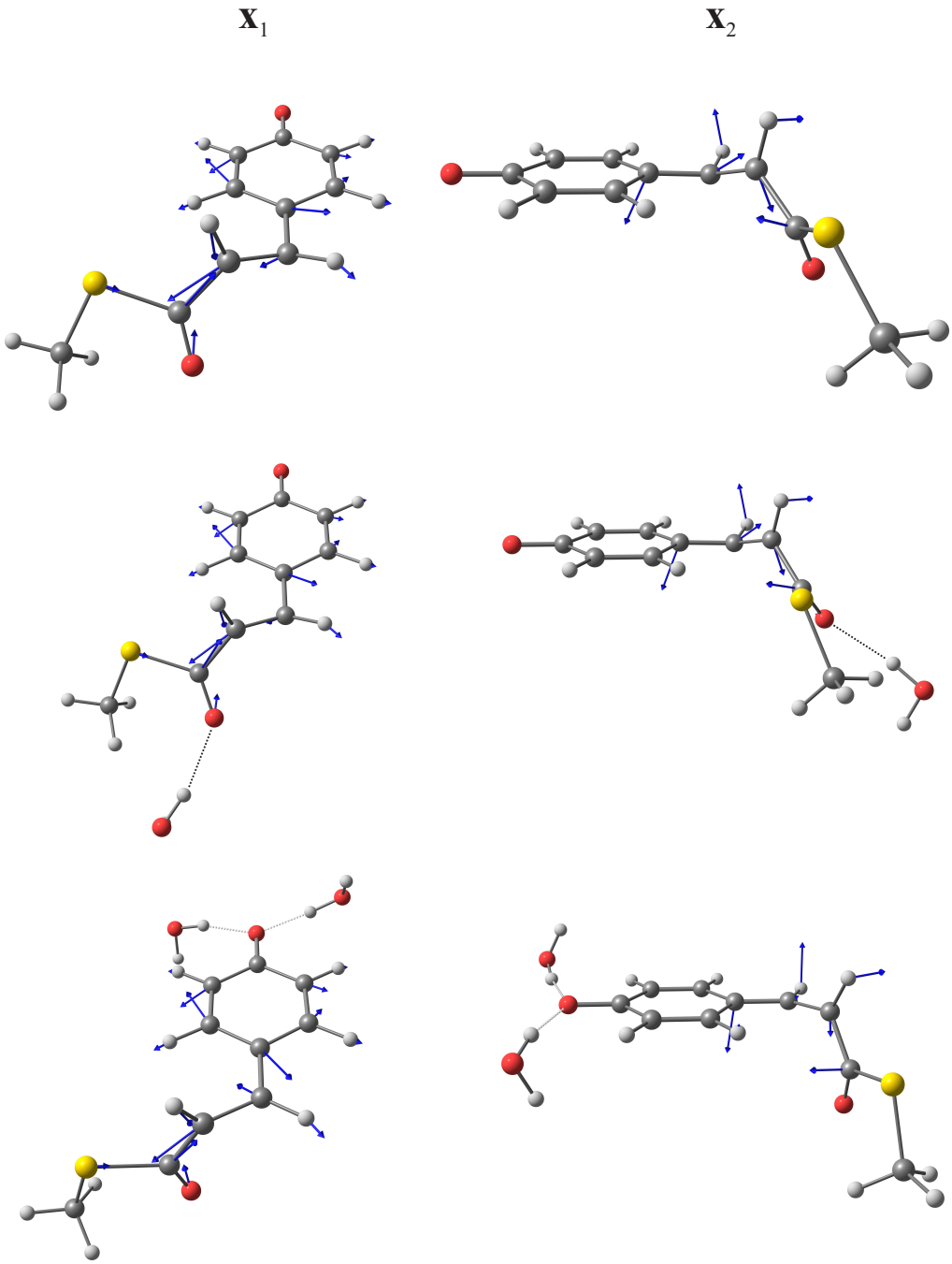


Figure S.2: Gradient difference ($\mathbf{x}_1$) and derivative coupling ($\mathbf{x}_2$) vectors at the β-CoIn in models **1**, **2** and **3**, from top to bottom, respectively.

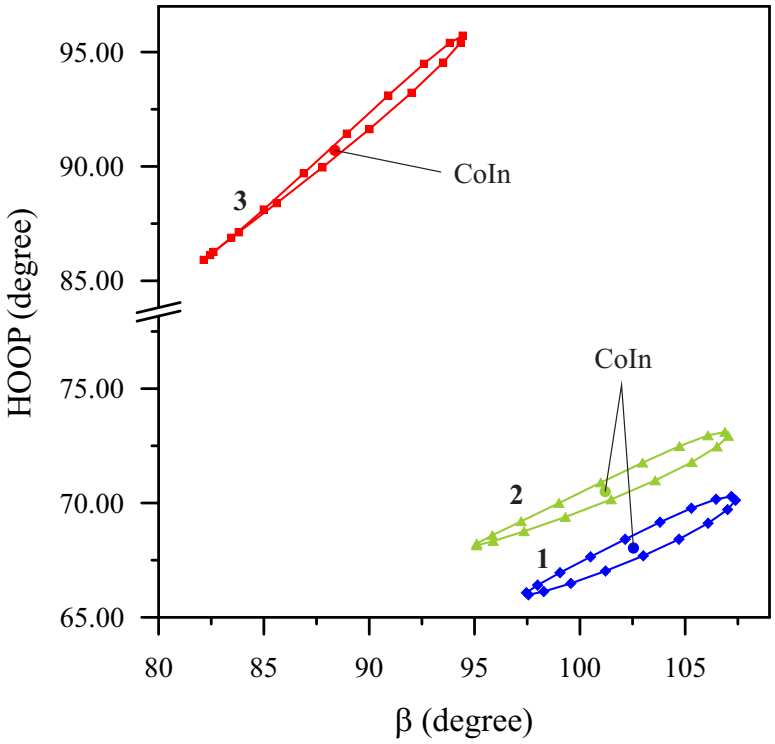


Figure S.3: Changes in the β-torsion and hydrogen out-of-plane (HOOP) coordinate along the loop of radius 0.005 Å for models **1** (blue), **2** (green) and **3** (red).