Supporting Information

Insights into Dissociative Electron Transfer in Esterified Shikonin Semiquinones by in-situ ESR / UV-Vis spectroelectrochemistry

By

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1. Internal coordinates as Z-matrices and calculated harmonic frequencies obtained for the minimum energy conformers for the semiquinone structure for shikonin and isovalerylshikonin at the BandHLYP/6-311++G(2d,2p) level considering solvation by the Marenich, Cramer and Truhlar model

Table S1. Internal coordinates as Z-matrices for shikonin semiquinone

Atom number	Symbol	NA	Bond	NB	Angle	NC	Dihedral
1	C						
2	C	1	1.4176411				
3	C	2	1.4520041	1	117.482651		
4	C	3	1.4144305	2	119.967898	1	-0.0540349
5	C	4	1.4524636	3	120.52818	2	-0.0129488
6	C	1	1.3694245	2	123.237834	3	0.0574528
7	H	1	1.0767193	6	119.956696	5	179.850195
8	C	3	1.4066512	2	120.373866	1	-179.973476
9	C	4	1.4081416	3	119.286797	2	-179.983535
10	C	9	1.3806791	4	119.827106	3	0.1262444
11	C	8	1.3807284	3	119.788034	2	179.89796
12	H	10	1.0768706	9	118.887702	4	179.855186
13	H	11	1.0768158	8	119.046	3	-179.895928
14	C	6	1.5103536	1	121.582084	2	179.018063
15	H	14	1.0872974	6	107.976072	1	142.853911
16	C	14	1.5276951	6	111.32285	1	-98.3496925
17	H	16	1.0848058	14	108.261297	6	64.5967154
18	H	16	1.0878485	14	106.926699	6	-50.5663728
19	C	16	1.49703	14	113.046583	6	-170.581043
20	H	19	1.0827609	16	114.314661	14	54.3593643
21	C	19	1.330059	16	128.467375	14	-126.829586
22	C	21	1.5015569	19	120.87031	16	-178.614508
23	H	22	1.0891504	21	110.788924	19	-121.526653
24	H	22	1.0851879	21	111.873374	19	-0.5602025
25	H	22	1.0891711	21	110.789767	19	120.38552
26	C	21	1.4998953	19	124.988975	16	1.1230867
27	H	26	1.0823714	21	113.441821	19	1.6178393
28	H	26	1.0888956	21	110.23403	19	122.979688
29	H	26	1.0891764	21	110.29479	19	-119.708186
30	O	14	1.4161793	6	112.248365	1	22.0166203
31	H	30	0.9537122	14	108.836454	6	63.7378652
32	O	9	1.3457176	4	121.131026	3	-179.951092
33	H	32	0.9817713	9	105.722581	4	-0.1280787
34	O	8	1.3455372	3	120.99007	2	-0.085006
35	H	34	0.9819549	8	105.773487	3	0.0851185
36	O	5	1.2667774	4	120.64389	3	-179.874175
37	O	2	1.266055	1	121.686361	6	-179.924235

Table S2. List of calculated harmonic frequencies of each vibrational normal mode for shikonin semiquinone

Mode	Frequency / cm^{-1}
1	14.75
2	30.52
3	39.48
4	58.45
5	83.47
6	101.28
7	110.66
8	142.84
9	157.29
10	172.60
11	201.98
12	205.86
13	237.97
14	282.43
15	304.12
16	314.76
17	324.03
18	344.98
19	393.99
20	399.20
21	407.34
22	432.03
23	447.73
24	450.97
25	476.83
26	490.29
27	494.97
28	505.09
29	512.07
30	554.95
31	571.06
32	622.75
33	665.47
34	708.99
35	724.36
36	741.82
37	761.07
38	796.33
39	814.65

40	824.57
41	865.15
42	871.50
43	871.90
44	881.91
45	927.06
46	941.28
47	960.33
48	983.36
49	989.03
50	997.24
51	1034.82
52	1051.81
53	1076.87
54	1084.59
55	1126.64
56	1144.20
57	1164.11
58	1181.89
59	1210.33
60	1220.94
61	1278.90
62	1288.60
63	1293.13
64	1314.91
65	1332.34
66	1339.59
67	1347.32
68	1356.84
69	1400.93
70	1422.45
71	1431.05
72	1447.17
73	1454.58
74	1458.69
75	1464.83
76	1504.11
77	1506.06
78	1512.98
79	1517.33
80	1521.36
81	1522.12
82	1526.74

83	1548.13
84	1589.09
85	1604.95
86	1652.15
87	1724.94
88	1732.49
89	1801.21
90	3090.50
91	3097.42
92	3124.00
93	3126.49
94	3135.70
95	3138.15
96	3177.32
97	3181.46
98	3197.72
99	3211.16
100	3268.22
101	3274.84
102	3282.32
103	3330.81
104	3339.08
105	3984.79

Table S3. Internal coordinates as Z-matrices for isovalerylshikonin semiquinone

Atom Number	Symbol	NA	Bond	NB	Angle	NC	Dihedral
1	C						
2	C	1	1.4170897				
3	C	2	1.4527511	1	117.460954		
4	C	3	1.4143084	2	120.020245	1	-0.0617961
5	C	4	1.4528805	3	120.52821	2	-0.159178
6	C	1	1.3693789	2	123.074082	3	0.010958
7	H	1	1.0768886	6	120.252784	5	179.853503
8	C	3	1.4061218	2	120.325858	1	179.888312
9	C	4	1.4076033	3	119.321356	2	179.825228
10	C	9	1.381089	4	119.795563	3	0.0702997
11	C	8	1.3810758	3	119.774833	2	-179.847518
12	H	10	1.0768191	9	118.884784	4	179.964833
13	H	11	1.0767607	8	119.025336	3	-179.989117
14	C	6	1.5054841	1	121.733704	2	178.422129
15	H	14	1.0807487	6	108.964253	1	147.736512
16	C	14	1.5260584	6	112.205397	1	-90.5893063
17	H	16	1.0841582	14	108.648375	6	63.7919756
18	H	16	1.0881083	14	106.440611	6	-51.0995031
19	C	16	1.4971491	14	112.875102	6	-170.850106
20	H	19	1.0824708	16	114.300455	14	58.3555845
21	C	19	1.3300383	16	128.382247	14	-122.16782
22	C	21	1.5011715	19	120.770448	16	-179.294566
23	H	22	1.0889888	21	110.705983	19	-121.14207
24	H	22	1.0849895	21	111.906245	19	-0.1227563
25	H	22	1.0890609	21	110.775626	19	120.848757
26	C	21	1.4996564	19	125.08957	16	0.5117455
27	H	26	1.0823871	21	113.492045	19	2.0134756
28	H	26	1.0887646	21	110.153351	19	123.414746
29	H	26	1.0890879	21	110.224129	19	-119.314668
30	O	14	1.4366633	6	110.801946	1	28.409374
31	O	9	1.3455904	4	121.191555	3	179.999507
32	H	31	0.9811835	9	105.794243	4	-0.2260511
33	O	8	1.3453857	3	121.030989	2	0.1261379
34	H	33	0.9817309	8	105.786107	3	-0.0438685
35	O	5	1.2660195	4	120.757857	3	-179.499678
36	O	2	1.2655725	1	121.669465	6	179.996474
37	C	30	1.3292694	14	118.721869	6	83.3517846
38	C	37	1.5016778	30	111.432226	14	-175.898633
39	H	38	1.0861354	37	108.922684	30	-31.3675591
40	H	38	1.0900691	37	105.314297	30	82.483874

41	C	38	1.5248368	37	114.53502	30	-156.380398
42	H	41	1.0872926	38	107.7515	37	-49.4115609
43	C	41	1.5240725	38	111.364854	37	69.2932377
44	H	43	1.086486	41	111.75587	38	-57.5199484
45	H	43	1.0886902	41	110.700987	38	62.8144456
46	H	43	1.0870351	41	110.837663	38	-177.648079
47	C	41	1.5232241	38	110.056255	37	-167.278582
48	H	47	1.0870041	41	110.874835	38	179.402814
49	H	47	1.0886423	41	111.081462	38	-60.9182978
50	H	47	1.0871477	41	111.319428	38	59.2936116
51	O	37	1.1995096	30	123.39503	14	2.2477938

Table S4. List of calculated harmonic frequencies for each vibrational normal mode for isovalerylshikonin semiquinone

Mode	Frequency / cm^{-1}
1	18.09
2	19.61
3	31.64
4	34.03
5	38.35
6	43.11
7	54.89
8	86.60
9	92.69
10	111.9
11	119.66
12	127.60
13	143.29
14	153.39
15	160.89
16	194.06
17	204.71
18	232.58
19	234.77
20	245.97
21	252.42
22	275.04
23	310.58
24	317.18
25	338.76
26	349.13
27	378.29
28	392.66

29	397.37
30	405.28
31	418.72
32	436.14
33	443.64
34	450.34
35	463.67
36	486.01
37	490.52
38	505.32
39	511.38
40	518.26
41	563.20
42	572.79
43	618.55
44	630.64
45	668.97
46	714.43
47	726.37
48	744.62
49	761.30
50	770.24
51	806.36
52	814.82
53	825.81
54	863.92
55	868.52
56	874.01
57	884.28
58	884.44
59	925.08
60	929.31
61	935.84
62	960.01
63	964.63
64	983.60
65	986.66
66	989.23
67	996.32
68	1006.63
69	1030.90
70	1045.37
71	1053.67
72	1082.29
73	1102.34

74	1122.15
75	1143.41
76	1165.56
77	1171.60
78	1182.43
79	1183.87
80	1223.06
81	1233.62
82	1250.50
83	1265.26
84	1284.56
85	1293.46
86	1305.46
87	1311.22
88	1315.44
89	1333.20
90	1343.83
91	1356.91
92	1374.82
93	1403.13
94	1408.38
95	1411.37
96	1430.89
97	1438.34
98	1448.82
99	1450.91
100	1457.97
101	1459.00
102	1464.22
103	1465.40
104	1493.06
105	1504.98
106	1509.82
107	1514.59
108	1517.80
109	1522.2
110	1524.21
111	1525.10
112	1526.39
113	1527.72
114	1535.29
115	1540.37
116	1547.63
117	1589.89
118	1606.17

119	1653.35
120	1725.26
121	1733.65
122	1800.86
123	1840.52
124	3092.77
125	3095.63
126	3099.03
127	3099.98
128	3113.18
129	3122.97
130	3123.77
131	3138.44
132	3140.8
133	3157.11
134	3162.59
135	3166.98
136	3170.6
137	3173.22
138	3181.49
139	3183.84
140	3200.5
141	3210.79
142	3217.09
143	3268.27
144	3273.52
145	3282.32
146	3336.53
147	3350.65

2. Summary of calculated total energies for obtaining $\Delta G_{cleavage}$ in equation 1.

Calculated Total Energy	E / eV
R^-	-9427.55
$Q^{\bullet-}$	-34444.77
Q^-	-25020.35

3. References

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