Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Controlling electron emission from the photoactive yellow protein chromophore by substitution at the coumaric acid group

Michael A. Parkes, Ciara Phillips, Michael J. Porter, and Helen H. Fielding*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

E-mail: h.h.fielding@ucl.ac.uk

*To whom correspondence should be addressed

Supplementary Information

S-Methyl (*E*)-3-(4-hydroxyphenyl)prop-2-enethioate (*p*CT)

A solution of *p*CA (1.98 g, 12.0 mmol) in DMF (10 mL) was added to a solution of dicyclohexylcarbodiimide (1.25 g, 6.1 mmol) in DMF (10 mL) under argon, and the mixture heated to 90 °C for 2 h. The resulting yellow suspension was cooled to room temperature then filtered through a plug of cotton wool into a stirred suspension of sodium methanethiolate (1.07 g, 15.2 mmol) in DMF (5 mL). The reaction mixture was stirred vigorously for 22 h to give a deep orange gelatinous mixture. Removal of the solvent under reduced pressure at 50 °C afforded an orange-red slurry which was partitioned between ethyl acetate (50 mL) and saturated aqueous ammonium chloride (50 mL). The aqueous layer was further extracted with ethyl acetate (50 mL), then the combined organic extracts washed with saturated aqueous ammonium chloride (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$) and concentrated to yield a viscous yellow oil. Flash chromatography (SiO_2; EtOAc:petroleum ether 20:80 to 50:50) then gave the desired product (0.45 g, 38%) as a yellow solid.

NMR: δ_H (300 MHz, CD_3OD) 7.55 (1H, d, *J* 15.6 Hz, COCH=CH), 7.48 (2H, d, *J* 8.7 Hz Ar-H), 6.81 (2H, d, *J* 8.7 Hz, Ar-H), 6.68 (1H, d, *J* 15.6 Hz, COCH), 2.38 (3H, s, SCH_3).

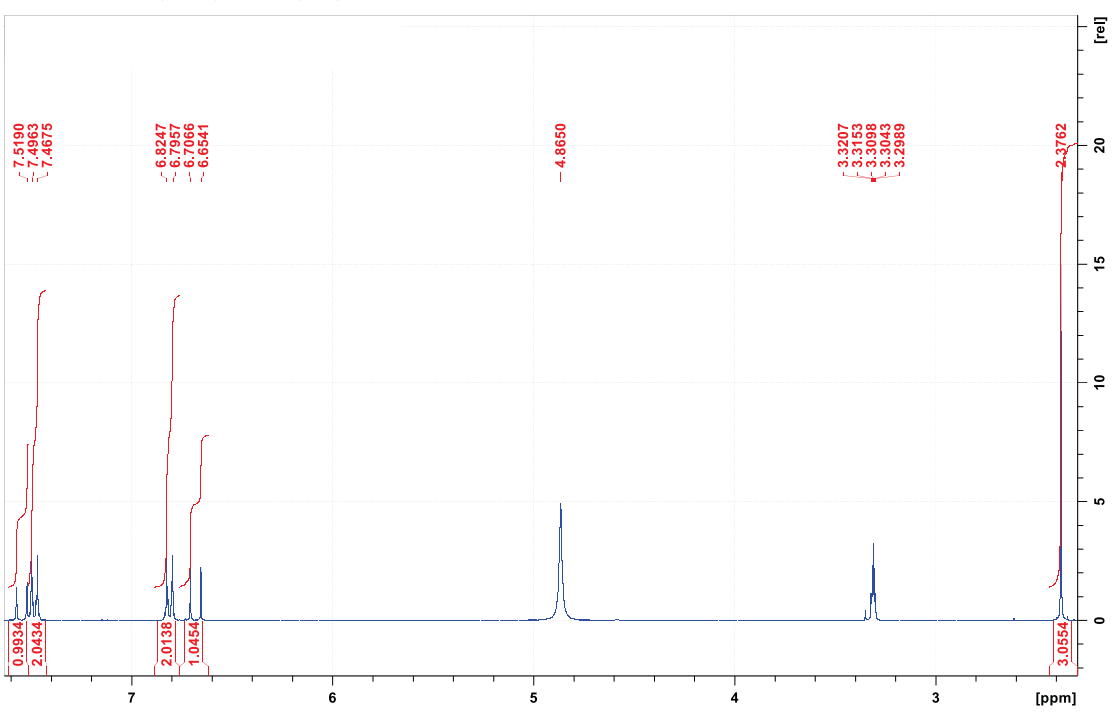

Figure 1: ^{1}H NMR of *p*CT.

Computational

Table 1: Z-matrix of the optimised geometry of the deprotonated pCA$^-$ anion using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.364819		
3	C	2	1		1.423504	122.201763	
4	C	3	2	1	1.421974	116.094622	-0.016519
5	C	4	3	2	1.367066	122.785959	0.016673
6	C	5	4	3	1.449073	122.000534	0.027062
7	H	1	2	3	1.083531	120.852789	179.988392
8	H	2	1	6	1.084104	119.007130	179.975085
9	H	4	3	2	1.086022	117.772033	-179.979843
10	H	5	4	3	1.083274	121.009102	-179.986934
11	C	3	2	1	1.415585	124.062470	179.998256
12	H	11	3	2	1.086855	115.487465	179.994787
13	C	11	3	2	1.370907	129.560329	-0.005931
14	H	13	11	3	1.080208	122.092029	0.002876
15	C	13	11	3	1.431626	121.272523	-179.998206
16	O	6	5	4	1.252894	123.089076	-179.915574
17	O	15	13	11	1.389452	112.281432	-179.972490
18	H	17	15	13	0.965836	104.193220	179.976495
19	O	15	13	11	1.225493	129.184204	-0.025883

Table 2: Z-matrix of the optimised geometry of the deprotonated *p*CA radical using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.367571		
3	C	2	1		1.433555	121.167544	
4	C	3	2	1	1.429611	118.447524	-0.006973
5	C	4	3	2	1.371144	121.540320	0.006867
6	C	5	4	3	1.460659	120.939617	0.014845
7	H	1	2	3	1.090002	121.799025	179.995409
8	H	2	1	6	1.089501	119.466757	179.987253
9	H	4	3	2	1.091163	118.363957	-179.990845
10	H	5	4	3	1.089991	121.929843	-179.995160
11	C	3	2	1	1.441443	122.970758	-179.999145
12	H	11	3	2	1.092820	116.564734	179.996550
13	C	11	3	2	1.360203	127.068214	-0.003142
14	H	13	11	3	1.088571	123.097628	0.000000
15	C	13	11	3	1.475594	120.257764	180.000000
16	O	6	5	4	1.247345	121.776409	-179.966756
17	O	15	13	11	1.361483	111.294543	179.998992
18	H	17	15	13	0.970881	106.860633	-179.999155
19	O	15	13	11	1.215698	126.160400	0.000776

Table 3: Z-matrix of the optimised geometry of the deprotonated pCE$^-$ anion using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.36775		
3	C	2	1		1.421343	122.7804484	
4	C	3	2	1	1.422745	116.0828776	0.00738
5	C	4	3	2	1.365486	122.211328	-0.0072
6	C	1	2	3	1.44903	122.0624418	0.010499
7	H	1	2	3	1.083347	120.9765615	-179.995
8	H	2	1	6	1.086114	119.449278	-179.99
9	H	4	3	2	1.084174	118.7789375	179.9922
10	H	5	4	3	1.08359	120.8306164	179.9954
11	O	6	1	2	1.251525	123.1370745	-179.965
12	C	3	2	1	1.417697	119.873963	-179.999
13	C	12	3	2	1.369139	129.5919675	-179.995
14	H	12	3	2	1.086789	115.395555	0.004002
15	H	13	12	3	1.080246	122.1296987	0
16	C	13	12	3	1.435914	121.2958365	180
17	O	16	13	12	1.387236	111.1184773	179.991
18	O	16	13	12	1.221165	128.8460926	0.007514
19	C	17	16	13	1.418608	115.3076939	-179.992
20	H	19	17	16	1.091137	111.3768739	-60.3728
21	H	19	17	16	1.088477	106.0322075	179.9967
22	H	19	17	16	1.091136	111.3770428	60.3658

Table 4: Z-matrix of the optimised geometry of the deprotonated *p*CE radical using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.361995		
3	C	2	1		1.422791	121.6409229	
4	C	3	2	1	1.426615	118.3032709	-0.0027
5	C	4	3	2	1.358448	121.25994	0.00272
6	C	1	2	3	1.455041	121.0336162	-0.00471
7	H	1	2	3	1.08114	121.9173433	179.9983
8	H	2	1	6	1.082772	120.148163	179.9958
9	H	4	3	2	1.081138	119.2394275	-179.997
10	H	5	4	3	1.081265	121.7785156	-179.998
11	O	6	1	2	1.239213	121.9065184	179.9881
12	C	3	2	1	1.434733	118.5951047	-180
13	C	12	3	2	1.350776	127.2595903	179.9983
14	H	12	3	2	1.084505	116.4221244	-0.00171
15	H	13	12	3	1.080011	123.0402036	0
16	C	13	12	3	1.474646	120.4127881	179.9997
17	O	16	13	12	1.348728	110.6790693	179.9967
18	O	16	13	12	1.208308	125.7187366	0.003429
19	C	17	16	13	1.435197	115.8679284	-179.997
20	H	19	17	16	1.088292	110.4157352	-60.3329
21	H	19	17	16	1.085059	105.6476105	-180
22	H	19	17	16	1.088293	110.4157545	60.33295

Table 5: Z-matrix of the optimised geometry of the deprotonated pCT^{-} anion using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.36566		
3	C	2	1		1.423705	122.7473	
4	C	3	2	1	1.424988	116.1511	0
5	C	4	3	2	1.363621	122.1506	0
6	C	1	2	3	1.450393	121.9924	0
7	H	1	2	3	1.083125	121.0657	180
8	H	2	1	6	1.08588	119.5402	179.9997
9	H	4	3	2	1.083913	118.8076	-180
10	H	5	4	3	1.083367	120.9046	-180
11	O	6	1	2	1.249421	123.0469	179.9992
12	C	3	2	1	1.412357	119.8011	180
13	C	12	3	2	1.375291	129.4906	-180
14	H	12	3	2	1.086313	115.4693	0
15	H	13	12	3	1.081615	121.5169	0
16	C	13	12	3	1.426879	121.5602	-180
17	O	16	13	12	1.219881	128.9482	0.001225
18	S	16	13	12	1.857417	111.2092	179.9991
19	C	18	16	13	1.81009	100.1585	180
20	H	19	18	16	1.08821	110.403	119.3013
21	H	19	18	16	1.088211	110.4031	-119.298
22	H	19	18	16	1.090749	106.498	0.001431

Table 6: Z-matrix of the optimised geometry of the deprotonated *p*CT radical using the B3LYP/6-311++G(3df,3pd) method

Row	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.361434		
3	C	2	1		1.423751	121.6622	
4	C	3	2	1	1.427349	118.2622	-0.00298
5	C	4	3	2	1.35802	121.2691	0.002989
6	C	1	2	3	1.455485	121.0382	-0.00492
7	H	1	2	3	1.081133	121.9224	179.9983
8	H	2	1	6	1.08279	120.1685	179.9956
9	H	4	3	2	1.08117	119.2791	-179.997
10	H	5	4	3	1.081274	121.781	-179.998
11	O	6	1	2	1.238647	121.9132	179.9873
12	C	3	2	1	1.432248	118.596	180
13	C	12	3	2	1.353884	127.3306	179.9985
14	H	12	3	2	1.084405	116.4213	-0.00118
15	H	13	12	3	1.081534	122.327	0
16	C	13	12	3	1.47303	120.7057	-179.999
17	O	16	13	12	1.210711	124.9631	-0.015
18	S	16	13	12	1.78664	112.1018	-179.986
19	C	18	16	13	1.808781	99.78794	179.9691
20	H	19	18	16	1.08695	106.6505	-179.997
21	H	19	18	16	1.086248	110.091	-60.4792
22	H	19	18	16	1.086248	110.0911	60.4852