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

Electronic Supplementary Information: The Antiradical Activity of Catecholamines and Metabolites of Dopamine: Theoretical and Experimental Study

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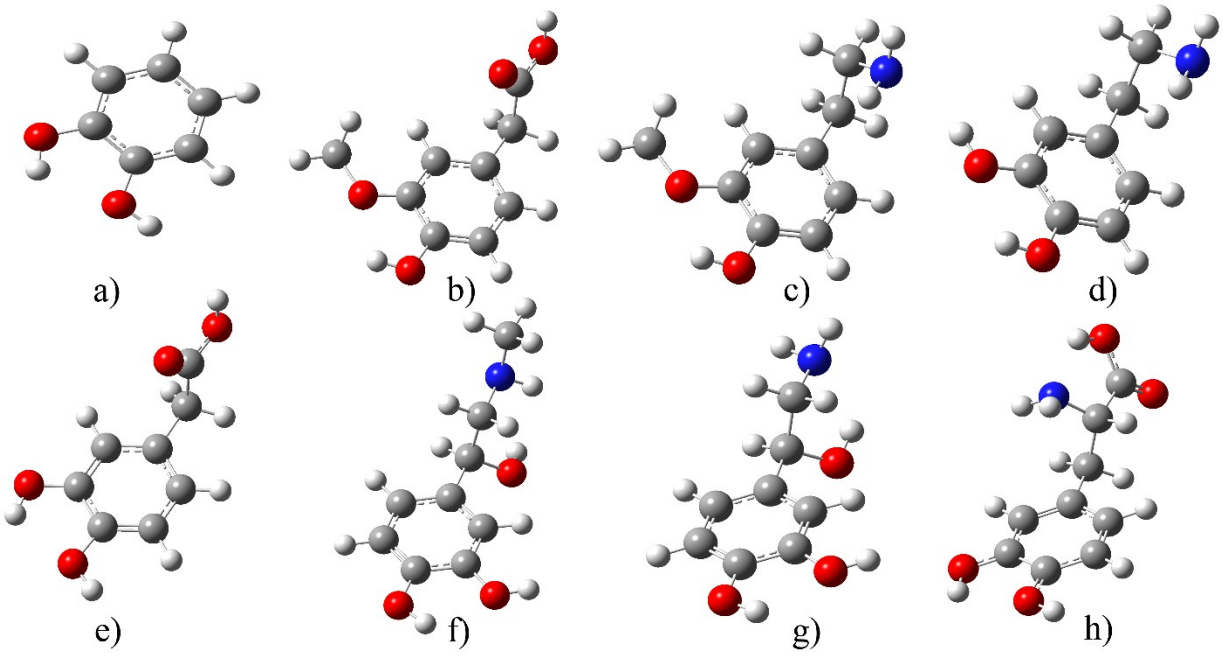

Fig. S1 The most stable conformers of investigated molecules in methanol at M062x/6-311++G(d,p) level of theory: a) catechol, b) homovanillic acid, c) 3-MT, d) dopamine, e) DOPAC, f) adrenaline, g) noradrenaline,h) L-DOPA.

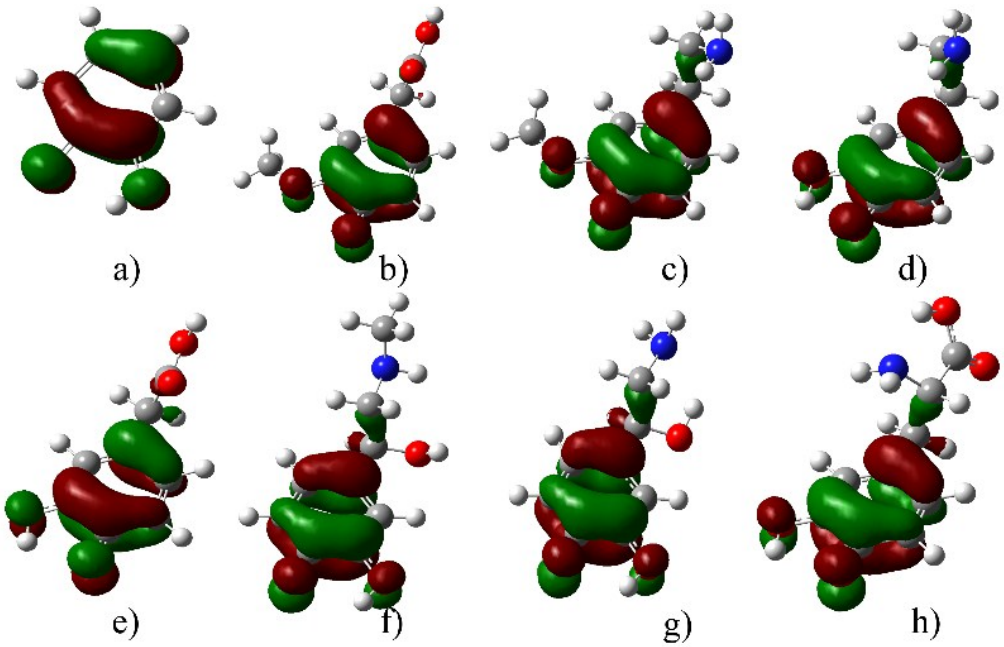

Fig. S2 SOMO orbitals of investigated molecules at M062x/6-311++G(d,p) level of theory: a) catechol, b) homovanillic acid, c) 3-MT, d) dopamine, e) DOPAC, f) adrenaline, g) noradrenaline, h) L-DOPA.

Table S3. NBO analysis parameters and interactions involving *p*-oxygen atom

Compound	Charge on oxygen atom	Intramolecular hydrogen bond - radical [kJ/mol]	Charge on oxygen atom	Intramolecular hydrogen bond – anion [kJ/mol]
Catechol	-0.653	1.04	-0.956	2.26
3-MT	-0.651	/	-0.946	/
Homovanillic acid	-0.645	/	-0.954	/
Dopamine	-0.661	1.04	-0.963	2.21
DOPAC	-0.657	1.05	-0.955	2.23
Adrenaline	-0.660	1.04	-0.952	2.26
Noradrenaline	-0.661	1.04	-0.953	2.29
L-DOPA	-0.662	1.07	-0.960	2.23

Table S4. Coordinates of atoms in L-DOPA-DPPH transition state

1	6	0	-4.245623	-1.703362	-0.452371
2	6	0	-3.440361	-0.581910	-0.561303
3	6	0	-2.012834	-0.645606	-0.560765
4	6	0	-1.505441	-1.979936	-0.677413
5	6	0	-2.284988	-3.107921	-0.576287
6	6	0	-3.659879	-2.956405	-0.425192
7	1	0	-5.323172	-1.590951	-0.414260
8	1	0	-1.833108	-4.092106	-0.626810
9	7	0	-1.133297	0.366102	-0.393290
10	7	0	-1.548558	1.567192	0.104654
11	6	0	-1.070314	2.708195	-0.549384
12	6	0	-0.755080	2.629563	-1.914654
13	6	0	-0.852750	3.903080	0.153709
14	6	0	-0.225823	3.739387	-2.562491
15	1	0	-0.932332	1.699520	-2.442182
16	6	0	-0.326432	5.002954	-0.509589
17	1	0	-1.065954	3.952587	1.215877
18	6	0	-0.006691	4.930440	-1.868088
19	1	0	0.003604	3.676108	-3.621771
20	1	0	-0.150183	5.921185	0.041515
21	1	0	0.401487	5.795976	-2.379679
22	6	0	-2.305230	1.605468	1.306635
23	6	0	-3.333890	2.543074	1.447461
24	6	0	-2.053146	0.668009	2.314440
25	6	0	-4.100797	2.547136	2.606804
26	1	0	-3.549566	3.229874	0.633927
27	6	0	-2.838832	0.676004	3.462105
28	1	0	-1.235692	-0.038889	2.201159
29	6	0	-3.860285	1.613751	3.614778
30	1	0	-4.907563	3.265386	2.708266
31	1	0	-2.644137	-0.050018	4.244732
32	1	0	-4.470361	1.612282	4.511888
33	7	0	-4.155147	0.670777	-0.813513
34	8	0	-5.266469	0.799894	-0.331866
35	8	0	-3.614109	1.484107	-1.545731
36	7	0	-4.503038	-4.141385	-0.309926
37	8	0	-3.948339	-5.226909	-0.327570
38	8	0	-5.704623	-3.968577	-0.200350
39	7	0	-0.084485	-2.209801	-0.977727
40	8	0	0.455197	-1.441659	-1.755373
41	8	0	0.445120	-3.183429	-0.475263
42	6	0	4.609836	-0.490539	-0.638970
43	6	0	4.110150	-1.554347	0.147453
44	6	0	3.801377	0.623707	-0.874387
45	6	0	2.835911	-1.507217	0.672893
46	1	0	4.740374	-2.421622	0.320817

47	6	0	2.520674	0.690639	-0.334741
48	1	0	4.167328	1.444495	-1.489391
49	6	0	2.004751	-0.384373	0.453947
50	1	0	2.426324	-2.329994	1.248957
51	8	0	0.795179	-0.312801	0.933495
52	1	0	-0.053367	0.071156	0.151597
53	8	0	1.674657	1.723009	-0.499575
54	1	0	1.989021	2.356381	-1.158719
55	6	0	6.018269	-0.528934	-1.173304
56	1	0	6.116700	0.170336	-2.009979
57	1	0	6.260344	-1.532692	-1.534454
58	6	0	7.063523	-0.152769	-0.101598
59	1	0	8.041317	-0.082090	-0.593300
60	7	0	6.825255	1.104237	0.604446
61	1	0	7.236442	1.897889	0.127325
62	1	0	5.829207	1.281084	0.718175
63	6	0	7.230308	-1.294357	0.920475
64	8	0	7.427383	-0.890646	2.172797
65	8	0	7.220846	-2.456271	0.599661
66	1	0	7.371010	0.088096	2.161026

Table S5. Coordinates of atoms in dopamine-DPPH transition state

1	6	0	-3.764384	-1.512598	-0.612319
2	6	0	-2.878811	-0.452258	-0.695208
3	6	0	-1.458759	-0.608869	-0.571288
4	6	0	-1.039323	-1.981572	-0.614969
5	6	0	-1.901794	-3.048338	-0.534532
6	6	0	-3.271448	-2.800495	-0.492309
7	1	0	-4.831029	-1.328232	-0.669204
8	1	0	-1.517632	-4.061720	-0.517417
9	7	0	-0.534499	0.342075	-0.344649
10	7	0	-0.926842	1.576293	0.095182
11	6	0	-0.337446	2.678165	-0.530826
12	6	0	0.108466	2.551115	-1.855978
13	6	0	-0.137625	3.882666	0.161562
14	6	0	0.750045	3.619164	-2.472044
15	1	0	-0.056448	1.615510	-2.377726
16	6	0	0.501476	4.940893	-0.470774
17	1	0	-0.454606	3.972906	1.194730
18	6	0	0.953141	4.818565	-1.787351
19	1	0	1.082498	3.515883	-3.500480
20	1	0	0.661460	5.865845	0.074197
21	1	0	1.449538	5.651136	-2.274920
22	6	0	-1.763922	1.670217	1.240984
23	6	0	-2.777306	2.632213	1.289350
24	6	0	-1.598759	0.759024	2.290306
25	6	0	-3.616244	2.686655	2.397634

26	1	0	-2.921499	3.301206	0.445356
27	6	0	-2.453359	0.817375	3.385242
28	1	0	-0.794800	0.029577	2.248606
29	6	0	-3.460734	1.780329	3.445983
30	1	0	-4.411970	3.423870	2.426827
31	1	0	-2.323650	0.110733	4.198532
32	1	0	-4.125450	1.818993	4.302639
33	7	0	-3.480450	0.829697	-1.061928
34	8	0	-4.629792	1.042619	-0.715568
35	8	0	-2.811889	1.584522	-1.750446
36	7	0	-4.199179	-3.919111	-0.399440
37	8	0	-3.723274	-5.040682	-0.333495
38	8	0	-5.391958	-3.664812	-0.388776
39	7	0	0.378568	-2.318009	-0.798059
40	8	0	1.034981	-1.606615	-1.538823
41	8	0	0.796610	-3.318245	-0.241962
42	6	0	5.154035	-0.791116	-0.163406
43	6	0	4.546363	-1.833438	0.579028
44	6	0	4.423052	0.363502	-0.440032
45	6	0	3.244216	-1.729427	1.014579
46	1	0	5.129683	-2.718332	0.805983
47	6	0	3.114260	0.492125	0.013462
48	1	0	4.875459	1.174390	-1.007663
49	6	0	2.489846	-0.566080	0.744227
50	1	0	2.753295	-2.532244	1.553513
51	8	0	1.249373	-0.441663	1.134693
52	1	0	0.523159	-0.015574	0.335511
53	8	0	2.334788	1.567341	-0.187790
54	1	0	2.742137	2.211362	-0.782832
55	6	0	6.582382	-0.904604	-0.624739
56	1	0	6.770499	-0.169494	-1.414472
57	1	0	6.754041	-1.896623	-1.061890
58	6	0	7.600386	-0.687694	0.507265
59	1	0	8.588027	-0.505584	0.057284
60	1	0	7.325066	0.215355	1.062133
61	7	0	7.584283	-1.813951	1.436722
62	1	0	8.076285	-2.612566	1.047261
63	1	0	8.035536	-1.578188	2.313466

Table S6. Coordinates of atoms in epinephrine-DPPH transition state

1	6	0	3.983385	1.785562	-0.805861
2	6	0	3.161326	0.673089	-0.845729
3	6	0	1.767853	0.720166	-0.517101
4	6	0	1.261673	2.058205	-0.403497
5	6	0	2.059184	3.177204	-0.365392
6	6	0	3.433337	3.025117	-0.527361
7	1	0	5.041287	1.680803	-1.018123
8	1	0	1.618426	4.157493	-0.225406

9	7	0	0.943839	-0.306198	-0.233754
10	7	0	1.457612	-1.546933	0.019321
11	6	0	0.826758	-2.620329	-0.617693
12	6	0	0.182796	-2.400039	-1.844962
13	6	0	0.773251	-3.888049	-0.016880
14	6	0	-0.504659	-3.440641	-2.458638
15	1	0	0.230153	-1.414756	-2.294121
16	6	0	0.084226	-4.917005	-0.644650
17	1	0	1.237557	-4.049265	0.949707
18	6	0	-0.560781	-4.702976	-1.866203
19	1	0	-0.992905	-3.264243	-3.411937
20	1	0	0.036541	-5.891256	-0.168449
21	1	0	-1.095509	-5.513028	-2.351102
22	6	0	2.470824	-1.698681	1.003040
23	6	0	3.491163	-2.635402	0.806623
24	6	0	2.472002	-0.874200	2.133916
25	6	0	4.502541	-2.755213	1.752358
26	1	0	3.504381	-3.230565	-0.101934
27	6	0	3.499717	-0.995184	3.063425
28	1	0	1.663480	-0.164278	2.285674
29	6	0	4.513497	-1.935582	2.880801
30	1	0	5.299580	-3.473304	1.590518
31	1	0	3.499928	-0.357423	3.941371
32	1	0	5.311233	-2.024511	3.610722
33	7	0	3.784495	-0.538907	-1.378522
34	8	0	4.973867	-0.707304	-1.173109
35	8	0	3.082644	-1.276628	-2.052196
36	7	0	4.294587	4.199239	-0.482486
37	8	0	3.763121	5.278872	-0.281836
38	8	0	5.491002	4.027635	-0.644548
39	7	0	-0.186701	2.304574	-0.377140
40	8	0	-0.891918	1.592138	-1.070165
41	8	0	-0.585613	3.242357	0.290590
42	6	0	-4.687624	0.234607	0.853251
43	6	0	-4.090196	1.343928	1.494831
44	6	0	-3.910016	-0.853456	0.475415
45	6	0	-2.733029	1.380872	1.725826
46	1	0	-4.712855	2.180683	1.800702
47	6	0	-2.541841	-0.839124	0.728779
48	1	0	-4.384883	-1.710442	0.006621
49	6	0	-1.917395	0.290120	1.345305
50	1	0	-2.249829	2.234428	2.188114
51	8	0	-0.626506	0.291737	1.543293
52	1	0	0.007752	-0.055423	0.617049
53	8	0	-1.705156	-1.845136	0.428562
54	1	0	-2.142296	-2.538577	-0.085235
55	6	0	-6.161309	0.262210	0.542719
56	1	0	-6.691693	0.629805	1.437598
57	6	0	-6.439886	1.218564	-0.635216

58	1	0	-6.190187	2.251744	-0.344656
59	1	0	-5.784639	0.926683	-1.462643
60	8	0	-6.616960	-1.025004	0.207572
61	1	0	-7.395006	-0.883328	-0.358453
62	7	0	-7.824998	1.061439	-1.060868
63	1	0	-7.924663	1.319425	-2.035664
64	6	0	-8.786061	1.791890	-0.241252
65	1	0	-8.551232	2.864023	-0.154358
66	1	0	-9.784717	1.682556	-0.668791
67	1	0	-8.812026	1.367016	0.766492

Table S7. Coordinates of atoms in norepinephrine-DPPH transition state

1	6	0	-3.841533	-1.513182	-0.797011
2	6	0	-2.929990	-0.472449	-0.838645
3	6	0	-1.542521	-0.635909	-0.521396
4	6	0	-1.150031	-2.012266	-0.408769
5	6	0	-2.037588	-3.060503	-0.368192
6	6	0	-3.395389	-2.794658	-0.524396
7	1	0	-4.887833	-1.319490	-1.003551
8	1	0	-1.679313	-4.074034	-0.229747
9	7	0	-0.632777	0.318874	-0.249814
10	7	0	-1.043396	1.590178	0.037430
11	6	0	-0.342797	2.626910	-0.586561
12	6	0	0.273662	2.384657	-1.823764
13	6	0	-0.197707	3.877187	0.035406
14	6	0	1.028482	3.385522	-2.424052
15	1	0	0.152141	1.413806	-2.290072
16	6	0	0.556556	4.866723	-0.580039
17	1	0	-0.644927	4.054067	1.007310
18	6	0	1.177461	4.630022	-1.809598
19	1	0	1.496051	3.193085	-3.384716
20	1	0	0.673985	5.827320	-0.088513
21	1	0	1.763952	5.409584	-2.284679
22	6	0	-2.029341	1.795332	1.040465
23	6	0	-2.999031	2.788871	0.869674
24	6	0	-2.055094	0.963492	2.165561
25	6	0	-3.987037	2.953781	1.834044
26	1	0	-2.994714	3.393280	-0.033111
27	6	0	-3.058428	1.131065	3.113979
28	1	0	-1.283128	0.210307	2.296819
29	6	0	-4.023636	2.125646	2.955475
30	1	0	-4.747395	3.714490	1.691509
31	1	0	-3.077488	0.487022	3.987124
32	1	0	-4.803704	2.250314	3.699129
33	7	0	-3.454890	0.788674	-1.362825
34	8	0	-4.630860	1.042971	-1.166466
35	8	0	-2.694298	1.481362	-2.020137
36	7	0	-4.350097	-3.893622	-0.478551

37	8	0	-3.908656	-5.013740	-0.280229
38	8	0	-5.528999	-3.625280	-0.637845
39	7	0	0.272893	-2.378710	-0.382733
40	8	0	1.031180	-1.734253	-1.084651
41	8	0	0.594039	-3.338960	0.295479
42	6	0	4.966684	-0.739943	0.854901
43	6	0	4.256239	-1.775254	1.503561
44	6	0	4.301144	0.405168	0.440458
45	6	0	2.900246	-1.677948	1.719776
46	1	0	4.790960	-2.663371	1.830937
47	6	0	2.932949	0.522382	0.665565
48	1	0	4.851981	1.203045	-0.048034
49	6	0	2.197985	-0.522567	1.307425
50	1	0	2.334508	-2.470745	2.196317
51	8	0	0.913267	-0.390499	1.503609
52	1	0	0.305795	-0.005550	0.579078
53	8	0	2.195965	1.589107	0.315189
54	1	0	2.700243	2.217345	-0.219785
55	6	0	6.444691	-0.918001	0.609472
56	1	0	6.903610	-1.285218	1.539837
57	6	0	6.716229	-1.940555	-0.502448
58	1	0	7.807405	-2.111921	-0.538246
59	1	0	6.246424	-2.892859	-0.233953
60	8	0	7.002687	0.339272	0.252475
61	1	0	7.961519	0.291317	0.332251
62	7	0	6.142370	-1.464081	-1.746997
63	1	0	6.576964	-0.592478	-2.031571
64	1	0	6.246427	-2.139470	-2.494619

Table S8. Partial charge and spin density values for the molecules of interest. RC, TS and PC are the reaction complex, transition state and product complex, respectively.

Molecule	Atom	Partial charge			Spin density		
		RC	TS	PC	RC	TS	PC
Dopamine	*p*-O	-0.735	-0.702	-0.586	0.001	0.174	0.347
	N	-0.285	-0.428	-0.410	0.298	0.079	0.001
	H	0.532	0.507	0.482	0.000	-0.012	0.000
Adrenaline	*p*-O	-0.775	-0.700	-0.586	0.004	0.178	0.348
	N	-0.318	-0.430	-0.403	0.318	0.077	0.001
	H	0.535	0.505	0.482	-0.001	-0.012	0.000
Noradrenaline	*p*-O	-0.760	-0.717	-0.583	0.002	0.178	0.351
	N	-0.288	-0.438	-0.412	0.320	0.080	0.001
	H	0.527	0.506	0.485	-0.001	-0.012	0.001
L-DOPA	*p*-O	-0.760	-0.698	-0.577	0.003	0.187	0.350
	N	-0.280	-0.434	-0.408	0.310	0.081	0.001
	H	0.536	0.500	0.482	-0.001	-0.012	0.000

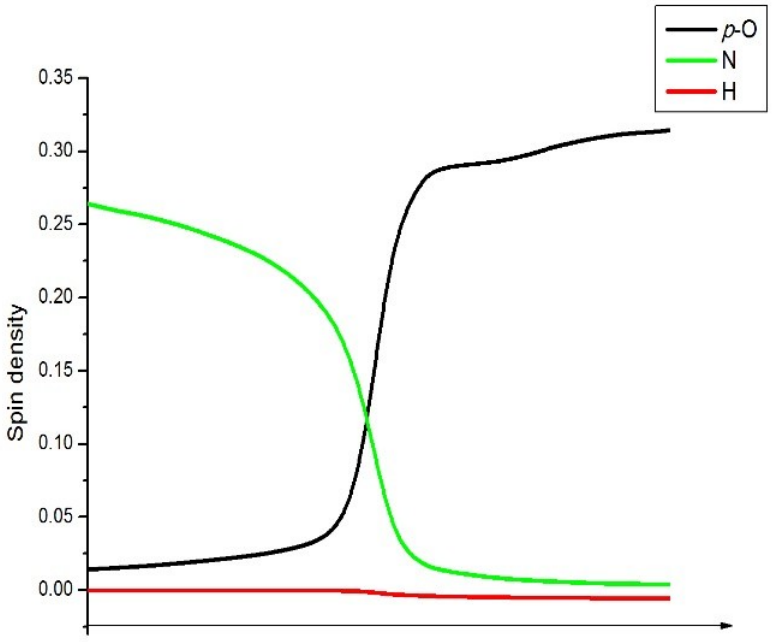

Fig. S9 Spin density change along the reaction coordinate for the relevant atoms for reaction between dopamine and DPPH.