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

Switching between cis and trans anions of 2-(2'-hydroxyphenyl)benzimidazole: A molecular rotation perturbed by chemical stabilization[§]

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Electronic Supplementary Information

[§]Dedicated to Prof. S. K. Dogra on his 74th birthday.

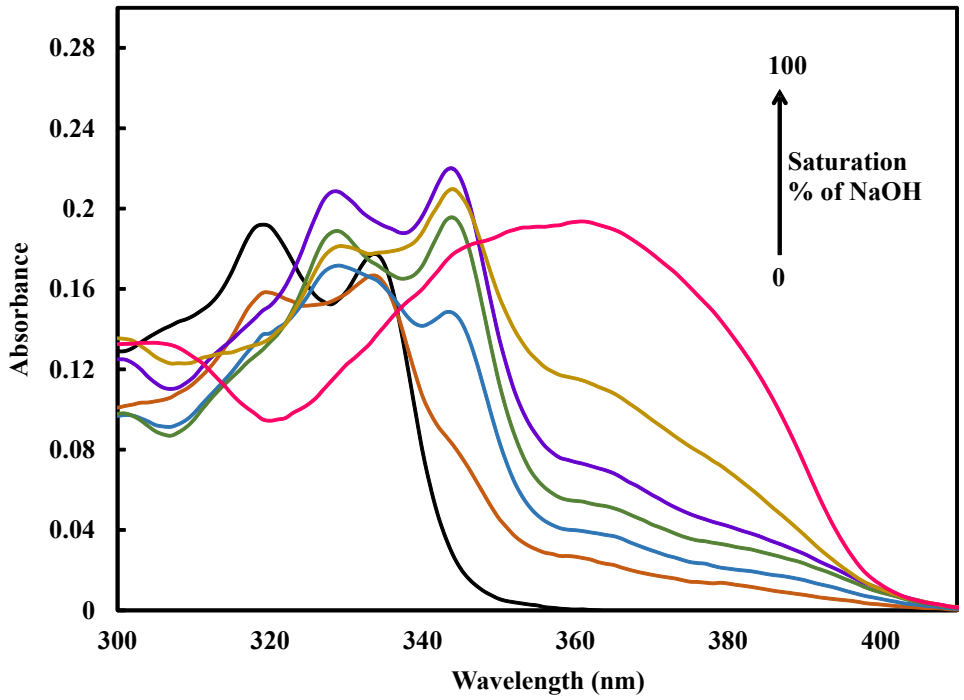


Fig. S1 Absorption spectra of HPBI in DMSO with increasing NaOH concentration.

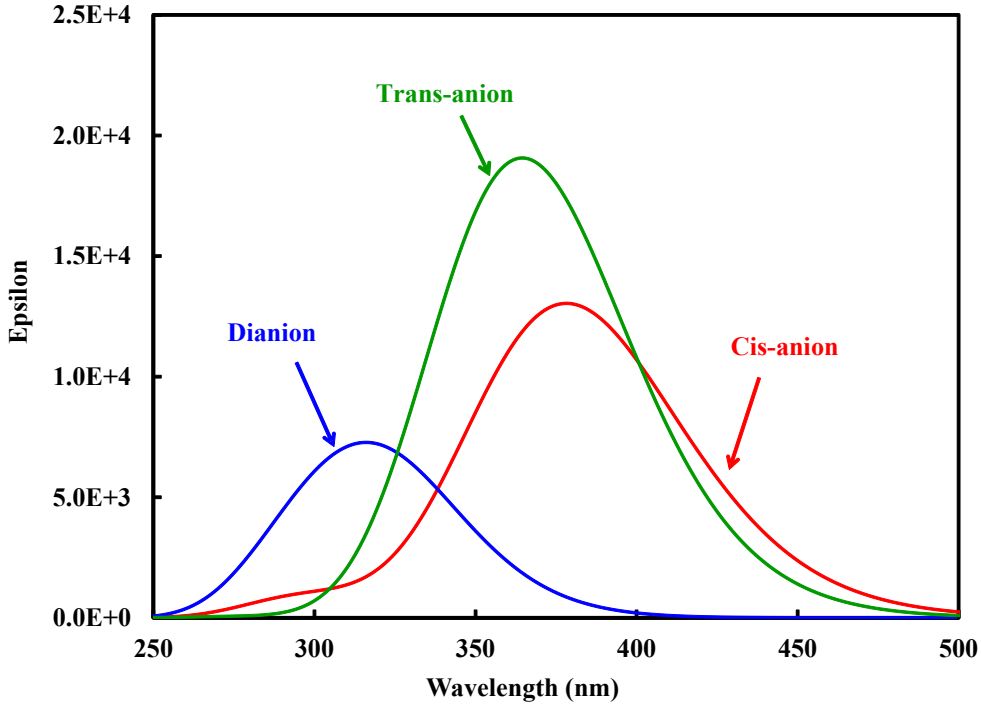


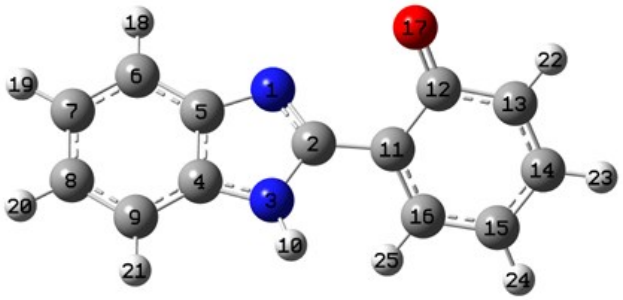
Fig. S2 Absorption spectra of cis-anion, trans-anion and dianion predicted by theoretical calculations.

Computational Data:

Table S1 The excitation energies (λ_{ab}) of cis-anion calculated using different functionals are compared with experimental value.

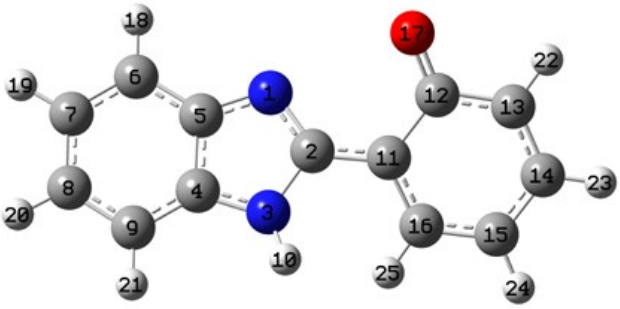
Functionals	λ_{ab} (nm)
CAM-B3LYP	327
PBE0	363
M062X	329
B3LYP-D3	378
B3LYP	378
Experimental	375

Table S2 XYZ coordinate of optimized cis-anion in ground state. (Optimized geometry is shown below).



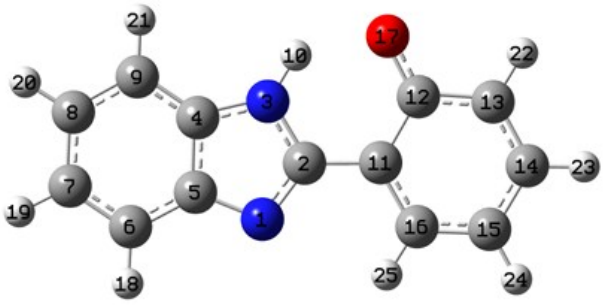
Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.6323	1.010844	-0.49686
2	6	0.124848	0.011786	-0.0568
3	7	-0.65216	-1.04073	0.407205
4	6	-1.98005	-0.69304	0.263478
5	6	-1.94428	0.604206	-0.30947
6	6	-3.14633	1.267587	-0.59959
7	6	-4.34615	0.618262	-0.30326
8	6	-4.36148	-0.67016	0.272702
9	6	-3.17579	-1.34967	0.565348
10	1	-0.2961	-1.87373	0.852765
11	6	1.588067	-0.09489	-0.07083
12	6	2.444668	1.022404	0.299721
13	6	3.859758	0.751802	0.226187
14	6	4.379381	-0.47965	-0.14195
15	6	3.528665	-1.55148	-0.4736
16	6	2.152824	-1.33702	-0.42901
17	8	2.008497	2.163358	0.693345
18	1	-3.13699	2.260156	-1.04091
19	1	-5.28911	1.112837	-0.51837
20	1	-5.3136	-1.14418	0.492772
21	1	-3.18744	-2.34195	1.006187
22	1	4.525932	1.57052	0.4906
23	1	5.458997	-0.61657	-0.17453
24	1	3.929457	-2.51537	-0.77197
25	1	1.487257	-2.15029	-0.71326

Table S3 XYZ coordinate of optimized cis-anion in excited state. (Optimized geometry is shown below).



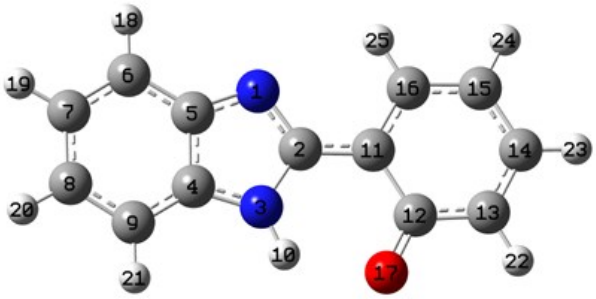
Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.64509	1.073054	-0.25599
2	6	0.136013	-0.00833	0.019663
3	7	-0.68366	-1.14462	0.20923
4	6	-1.99834	-0.74536	0.141914
5	6	-1.93581	0.650054	-0.17712
6	6	-3.1468	1.371911	-0.34899
7	6	-4.35476	0.680811	-0.19123
8	6	-4.39301	-0.68895	0.132908
9	6	-3.20311	-1.4311	0.309567
10	1	-0.36978	-2.02137	0.599105
11	6	1.562693	-0.13315	-0.02161
12	6	2.463564	1.031693	0.168218
13	6	3.879596	0.816818	0.070661
14	6	4.430941	-0.45649	-0.12197
15	6	3.57043	-1.55769	-0.2618
16	6	2.172102	-1.39678	-0.22958
17	8	2.001986	2.184099	0.454503
18	1	-3.128	2.43157	-0.58677
19	1	-5.2924	1.217441	-0.31599
20	1	-5.35246	-1.18488	0.250772
21	1	-3.22806	-2.4874	0.560708
22	1	4.512736	1.687474	0.219556
23	1	5.507882	-0.59378	-0.15616
24	1	3.982272	-2.5515	-0.41579
25	1	1.552045	-2.27006	-0.40797

Table S4 XYZ coordinate of optimized trans-anion in ground state. (Optimized geometry is shown below).



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.667966	-1.33005	0.00006
2	6	-0.13279	-0.25921	-0.00005
3	7	0.574917	0.919872	-0.00012
4	6	1.916028	0.606937	-0.00011
5	6	1.953177	-0.81646	0.000086
6	6	3.192673	-1.47628	0.000201
7	6	4.354702	-0.70178	0.000112
8	6	4.298945	0.708677	-0.00008
9	6	3.076266	1.38634	-0.0002
10	1	0.041234	1.800666	-0.00027
11	6	-1.58995	-0.24709	-7.3E-05
12	6	-2.30804	1.012976	-2.1E-05
13	6	-3.73867	0.915824	0.000085
14	6	-4.40162	-0.30288	0.000002
15	6	-3.6838	-1.51589	-0.00012
16	6	-2.29394	-1.46779	-0.00012
17	8	-1.71409	2.167844	0.000291
18	1	3.241061	-2.56176	0.00033
19	1	5.323925	-1.19283	0.00019
20	1	5.22356	1.27878	-0.00013
21	1	3.032533	2.471439	-0.00033
22	1	-4.29727	1.849113	0.000232
23	1	-5.4898	-0.31972	0.000054
24	1	-4.20396	-2.46913	-0.00016
25	1	-1.71662	-2.3884	-0.00018

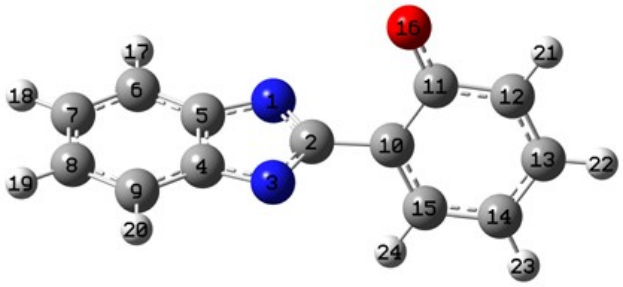
Table S5 XYZ coordinate of optimized trans-anion in excited state. (Optimized geometry is shown below).



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.67717	-1.28873	-3.8E-05
2	6	0.144534	-0.19321	-1.2E-05
3	7	-0.62193	0.977097	0.000013
4	6	-1.94459	0.632195	0.000011
5	6	-1.94907	-0.80487	-2.2E-05
6	6	-3.18915	-1.4932	-3.5E-05
7	6	-4.3661	-0.73179	-1.3E-05
8	6	-4.33966	0.676484	0.000018
9	6	-3.12224	1.389991	0.00003
10	1	-0.18177	1.890762	0.000025
11	6	1.565299	-0.23279	-9E-06
12	6	2.378071	1.009217	0.000025
13	6	3.80391	0.89052	0.000032
14	6	4.43981	-0.3578	0
15	6	3.657091	-1.53211	-3.5E-05
16	6	2.257776	-1.47737	-3.9E-05
17	8	1.807832	2.157486	0.000062
18	1	-3.21699	-2.57897	-0.00006
19	1	-5.3275	-1.23962	-2.2E-05
20	1	-5.27671	1.226806	0.000033
21	1	-3.10123	2.475386	0.000053
22	1	4.372492	1.816656	0.000062
23	1	5.523993	-0.42487	0.000004
24	1	4.146913	-2.5027	-5.9E-05
25	1	1.677721	-2.39353	-6.5E-05

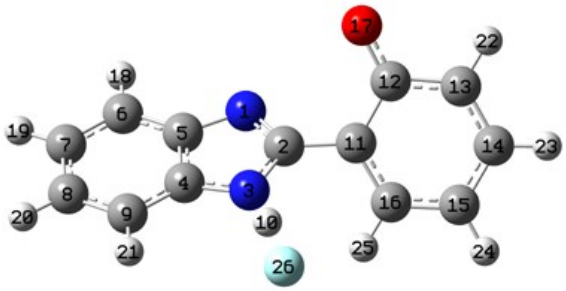
Table S6 XYZ coordinate of optimized di-anion in ground state.

(Optimized geometry is shown below).



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.62454	0.681304	-0.90675
2	6	0.089931	-0.07882	-0.03655
3	7	-0.63201	-0.82744	0.8389
4	6	-1.93711	-0.52688	0.515891
5	6	-1.93148	0.410852	-0.56899
6	6	-3.14155	0.885633	-1.10642
7	6	-4.34095	0.422528	-0.55735
8	6	-4.34626	-0.50131	0.514169
9	6	-3.15166	-0.98303	1.0581
10	6	1.578915	-0.14244	-0.06736
11	6	2.390549	0.955308	0.420353
12	6	3.81198	0.764217	0.319211
13	6	4.38575	-0.3985	-0.18978
14	6	3.580549	-1.45667	-0.637
15	6	2.188458	-1.30261	-0.56242
16	8	1.893016	2.035587	0.932009
17	1	-3.14529	1.59641	-1.93074
18	1	-5.28761	0.77751	-0.95817
19	1	-5.29673	-0.8414	0.918823
20	1	-3.16289	-1.69506	1.881322
21	1	4.446178	1.575019	0.674672
22	1	5.470856	-0.48368	-0.23593
23	1	4.018333	-2.36843	-1.03409
24	1	1.546162	-2.11176	-0.90814

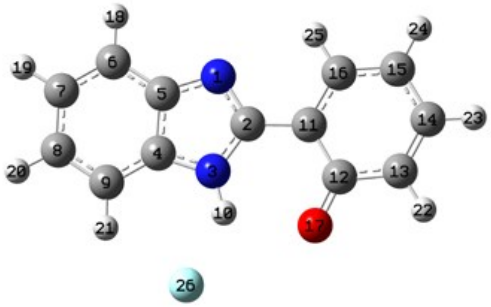
Table S7 XYZ coordinate of optimized NH-stabilized cis-anion in ground state. (Optimized geometry is shown below).



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.615765	-1.34036	-0.38884
2	6	-0.11795	-0.25614	-0.12056
3	7	0.652075	0.853004	0.149692
4	6	1.968197	0.456716	0.055088
5	6	1.929805	-0.92344	-0.28423
6	6	3.127738	-1.63455	-0.46292
7	6	4.333088	-0.95099	-0.29199
8	6	4.357139	0.41908	0.052209
9	6	3.176039	1.143703	0.23107
10	1	0.325598	1.836547	0.461476
11	6	-1.59062	-0.17315	-0.16653
12	6	-2.43251	-1.11279	0.554645
13	6	-3.84925	-0.91452	0.385429
14	6	-4.38572	0.109347	-0.3849
15	6	-3.5489	1.020681	-1.0526
16	6	-2.16727	0.860847	-0.92541
17	8	-1.97802	-2.04583	1.31717
18	1	3.112329	-2.68905	-0.72573
19	1	5.272795	-1.48047	-0.4245
20	1	5.313521	0.918726	0.180121
21	1	3.196175	2.196941	0.495442
22	1	-4.50528	-1.60737	0.909292
23	1	-5.46732	0.205668	-0.46806
24	1	-3.96054	1.823144	-1.65766
25	1	-1.50413	1.549043	-1.44556
26	9	0.040822	3.195118	0.919558

Table S8 XYZ coordinate of optimized NH-stabilized trans-anion

in ground state. (Optimized geometry is shown below).



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	-0.47896	-1.55946	0.000086
2	6	0.232721	-0.42058	-0.00013
3	7	-0.58319	0.691252	-0.00031
4	6	-1.88886	0.245694	-0.00016
5	6	-1.80245	-1.17078	0.000013
6	6	-2.97914	-1.93973	0.000239
7	6	-4.20453	-1.26966	0.000244
8	6	-4.27057	0.141853	0.000079
9	6	-3.11182	0.923875	-6.9E-05
10	1	-0.31683	1.687334	-0.00026
11	6	1.694627	-0.3827	-0.00014
12	6	2.429697	0.868104	0.000158
13	6	3.865787	0.748191	0.000449
14	6	4.51675	-0.475	0.000245
15	6	3.781858	-1.67867	-0.00025
16	6	2.392539	-1.6096	-0.00039
17	8	1.85583	2.019081	0.000106
18	1	-2.93218	-3.02561	0.000396
19	1	-5.12748	-1.84375	0.00038
20	1	-5.24271	0.627828	0.000121
21	1	-3.12465	2.008924	-0.00017
22	1	4.4334	1.676573	0.000753
23	1	5.605145	-0.5048	0.000416
24	1	4.28716	-2.64021	-0.00059
25	1	1.806392	-2.52384	-0.00067
26	9	-1.19329	3.397377	-0.00015