Supporting Information for:

Mechanism of degradation of nitrogenous heterocycle induced by a reductive radical: Decomposition of *sym*-triazine ring

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COMPUTATIONAL METHODS

The B3LYP method in the framework of DFT was employed to analyze the reaction mechanisms of degradation of CA.[1-4] The geometry optimizations for reactants, transition states, products and intermediates were carried out at the 6-31G(d) basis set.[5] Vibrational frequency calculations were performed to identify all of the stationary states as local minima (without imaginary frequency) or transition states as saddle point (only one imaginary frequency). Each transition state was verified exactly to connect with the designated reactants and products by running an intrinsic reaction coordinate analysis. For the radical intermediates, downhill methods was employed to help analyze the radical-radical couple. Finally, Using the conductive polarizable continuum model, all the optimized geometries were performed optimization again at the B3LYP/6-31+G(d,p) level to adjust the solvent effect.[6,7] Solvent is water herein. Calculations were carried out with the Gaussian 09 software package.[8]

Table S1. The reaction energy barriers (kcal/mol) of eight transition states at B3LYP/6-31+G(d,p), M06-2x/6-31+G(d,p)//B3LYP/6-31+G(d,p) and MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p) level.

Method	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8
B3LYP	4.96	9.79	13.32	38.27	14.58	18.54	14.53	59.62
M06-2x	8.62	12.04	11.87	34.34	13.92	17.64	11.19	58.87
MP2	13.81	21.56	19.93	41.69	22.2	26.84	20.73	62.01

To verify the reliability, we carried out the single point calculations for initial transition states using more precise methods, M06-2x/6-31+G(d,p) and MP2/6-31+G(d,p). As is shown in Table S1, the main channel is still the nitrogen atoms of CA1 reacting with •H rather than •OH. Furthermore, the relative energy barriers for other reaction channels have no change, which shows the reliability of our conclusions based on B3LYP. Thus, method of B3LPY in the 6-31+G(d,p) level is suitable for our systems. Three color was used to label these eight channels according to barrier level. Especially we can find the nitrogen atoms of CA reacting with •OH (TS4 or TS8) need climb quite high energy barrier, which also explains the results are not good to decompose the CA only employed •OH in early experiments.

EXPERIEMNTS

The γ photon irradiation experiment need not introduce any foreign matter, like initiator, catalyst and etc, which is good choice to produce the clear oxidative and reductive free radicals. Here, to confirm the transformation of the organic nitrogen, scavenger of reductive free radicals (•H) was employed to evaluate mineralization of organic nitrogen for different compounds (cyauric acid, as well as primidone and bezafibrate). To clearly reveal the transformation mechanism of organic nitrogen, all the experimental groups and control groups (no irradiation) were saturated with N_2 or N_2O prior to degrade. N_2 has a function, ruling out the influence of the air, such as O_2 and NH_3. The mineralized ions (NH_4^+) degraded from compounds were identified by ion chromatography system (Dionex ICS1100). The detection of NO_3^- in the samples was accomplished by anionic column. There are no NO_3^- been detected, that is to be expected. For measurement of ammonium, the eluent with a flow rate of 1 mL/min in the cationic column was 20mM methanesulphonic acid. The injection volume was 25 μL in all samples.

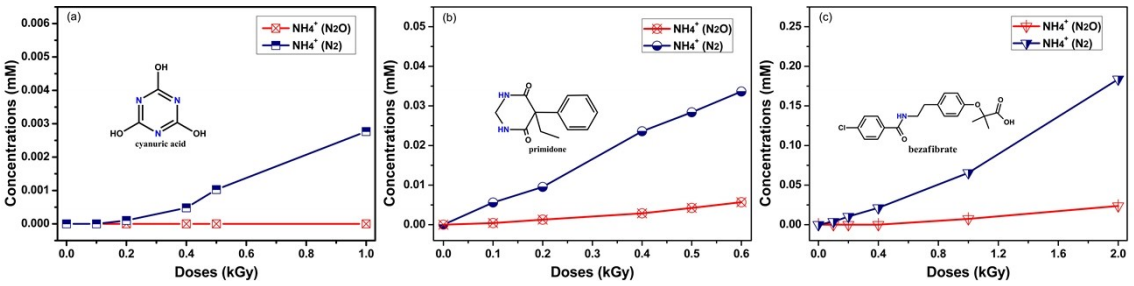

Figure S1. Concentration profiles of NH_4^+ in two kind of radical condition during the γ photon irradiation of cyauric acid, primidone and bezafibrate solution. The time of γ photo irradiation is 4h for each sample.

We herein investigated three different organics (cyauric acid, primidone and bezafibrate), which all contain organic nitrogen we concerned. As shown in Figure S1 (a), with the processes of irradiation, cyauric acid didn't decompose to give NH_4^+ when N_2O scavenge the •H. While some NH_4^+ gradually produced in initial irradiation in N_2 protective solution, which suggested •H is an effective radical to break C-N bonds. The consistent results shown in Figure S1 (b) and (c). The heterocycle and C-N chain were effectively broken with participation of •H for primidone and bezafibrate. Here, Only one nitrogen atom exist in molecular of bezafibrate, thus the mineralization ions (NH_4^+) is a good identification for the specificity of •H.

COORDINATES

TS1 (only one imaginary Frequencies -1170.1927)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.586350	-1.138487	-0.041828
2	7	0	1.349664	-0.018616	0.011881
3	7	0	-0.738608	-1.180347	-0.015551
4	6	0	0.618257	1.121641	-0.041880
5	6	0	-1.327349	0.019924	0.011516
6	7	0	-0.704764	1.203039	-0.019391
7	8	0	1.345730	2.236012	-0.059779
8	8	0	1.220565	-2.309289	-0.059551
9	8	0	-2.661469	0.070458	0.048469
10	1	0	-3.008039	-0.837678	0.057944
11	1	0	0.747465	3.002695	-0.045497
12	1	0	2.180688	-2.161441	-0.089199
13	1	0	2.233690	-0.028025	1.238218

TS2 (only one imaginary Frequencies -1124.3324)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.645244	1.131691	-0.006031
2	7	0	-0.684958	1.195469	-0.017695
3	7	0	1.392371	0.022271	0.021640
4	6	0	-1.282601	-0.021199	0.082856
5	6	0	0.681599	-1.111423	-0.005220
6	7	0	-0.645355	-1.218574	-0.020611
7	8	0	-2.611410	-0.009367	-0.147372
8	8	0	1.330005	2.276497	-0.039834
9	8	0	1.351416	-2.265157	-0.034488
10	1	0	2.304135	-2.071829	-0.052591
11	1	0	-2.931312	-0.927226	-0.149766
12	1	0	0.699269	3.016425	-0.044984
13	1	0	-1.332036	-0.021728	1.707932

TS3 (only one imaginary Frequencies -531.7447)

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.527684	1.258591	-0.141078
2	7	0	-0.778779	0.969945	-0.364648
3	7	0	1.501911	0.387504	0.028621
4	6	0	-1.071837	-0.375593	-0.235698
5	6	0	1.100747	-0.914078	-0.017921
6	7	0	-0.120403	-1.361115	-0.171739
7	8	0	-1.448023	-0.049371	1.501568
8	1	0	-2.179805	0.596094	1.468261
9	8	0	-2.241447	-0.720452	-0.796679
10	8	0	0.865313	2.545905	-0.130149
11	8	0	2.066813	-1.827325	0.091193
12	1	0	2.920460	-1.369613	0.174488
13	1	0	-2.306532	-1.690007	-0.791419
14	1	0	0.065960	3.085615	-0.256264

TS4 (only one imaginary Frequencies -332.9754)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.292721	-1.237842	0.284587
2	7	0	-1.030099	0.031419	0.312610
3	7	0	1.033464	-1.193390	0.022797
4	6	0	-0.301439	1.171487	0.059357
5	6	0	1.614196	-0.027209	-0.002980
6	7	0	0.996821	1.208031	0.026482
7	8	0	-2.343282	-0.013581	-0.205193
8	1	0	-2.915424	0.202298	0.551038
9	8	0	-1.035837	2.266599	-0.093346
10	8	0	-0.977862	-2.307196	-0.214707
11	8	0	2.959891	0.064651	-0.082046
12	1	0	3.323886	-0.835208	-0.096089
13	1	0	-0.434869	3.009568	-0.277506
14	1	0	-1.918386	-2.221484	0.005889

TS5 (only one imaginary Frequencies -1152.1019)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.737378	-1.237408	-0.011882
2	7	0	1.362173	0.000018	0.038408
3	7	0	-0.640938	-1.169029	-0.081488
4	6	0	0.737345	1.237427	-0.011882
5	6	0	-1.410266	-0.000018	0.070760
6	7	0	-0.640968	1.169011	-0.081497
7	8	0	1.355350	2.291193	-0.013309
8	8	0	1.355411	-2.291157	-0.013313
9	8	0	-2.644870	-0.000033	-0.102111
10	1	0	-1.143126	2.049085	-0.051654
11	1	0	-1.143070	-2.049119	-0.051642
12	1	0	2.374656	0.000032	0.079175
13	1	0	-1.564192	-0.000015	1.644040

TS6 (only one imaginary Frequencies -1559.8843)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.675688	-1.229843	-0.060534
2	7	0	0.698424	-1.158894	0.002316
3	7	0	-1.320658	0.000000	0.331646
4	6	0	1.458985	0.000000	0.022161
5	6	0	-0.675688	1.229843	-0.060534
6	7	0	0.698424	1.158894	0.002316
7	8	0	2.683031	0.000000	0.030933
8	8	0	-1.324649	-2.254007	-0.213852
9	8	0	-1.324648	2.254007	-0.213852
10	1	0	1.205843	2.030132	-0.110649
11	1	0	-2.286889	0.000000	-0.002508
12	1	0	1.205843	-2.030132	-0.110649
13	1	0	-1.573656	0.000000	1.637468

TS7 (only one imaginary Frequencies -534.0402)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.960628	-1.236403	-0.035167
2	7	0	1.571133	-0.003130	0.141113
3	7	0	-0.378489	-1.157080	-0.363482
4	6	0	0.971541	1.235463	-0.025488

5	6	0	-1.145269	0.006951	-0.299901
6	7	0	-0.374464	1.168813	-0.332968
7	8	0	1.582599	2.288460	0.072869
8	8	0	1.563394	-2.293824	0.068489
9	8	0	-2.327678	0.020775	-0.800121
10	1	0	-0.864622	2.049664	-0.436856
11	1	0	-0.884615	-2.032593	-0.426530
12	1	0	2.560436	-0.008305	0.360446
13	8	0	-1.927001	-0.119559	1.297383
14	1	0	-2.390372	0.728139	1.444679

TS8 (only one imaginary Frequencies -578.6123)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.006867	-0.816419	-0.420327
2	7	0	0.246593	-1.343250	-0.212064
3	7	0	-1.168845	0.536029	0.111748
4	6	0	1.446567	-0.709669	0.133394
5	6	0	0.409951	1.414225	-0.479730
6	7	0	1.430456	0.665603	0.091213
7	8	0	2.435024	-1.360661	0.438383
8	8	0	-1.924676	-1.436078	-0.915233
9	8	0	0.387471	2.619679	-0.570422
10	1	0	2.293763	1.132229	0.359939
11	1	0	-1.875236	1.020282	-0.445809
12	1	0	0.336284	-2.338825	-0.388349
13	8	0	-1.914978	0.326851	1.429010
14	1	0	-1.272875	0.650476	2.084013

IM1 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.592321	-1.175157	-0.000798
2	7	0	-1.327897	0.016086	0.197978
3	7	0	0.696035	-1.205725	-0.003347
4	6	0	-0.567296	1.183406	0.018638
5	6	0	1.343767	-0.008710	0.137422
6	7	0	0.717984	1.211142	0.011663

7	8	0	-1.338402	2.276237	-0.081403
8	8	0	-1.298376	-2.315361	-0.123132
9	8	0	2.699963	0.020470	-0.068133
10	1	0	3.026867	-0.889983	-0.014270
11	1	0	-0.762814	3.049676	-0.203454
12	1	0	-2.206956	-2.215432	0.202862
13	1	0	-2.270337	0.057221	-0.179424

IM2 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.148233	1.411741	-0.417856
2	7	0	1.102967	0.673818	-0.478548
3	7	0	-1.289455	0.541357	-0.421318
4	6	0	1.146438	-0.584226	-0.017941
5	6	0	-1.093067	-0.678056	-0.031346
6	7	0	0.090943	-1.312420	0.249558
7	8	0	2.373561	-1.089157	0.123854
8	8	0	-0.090914	2.193463	0.783864
9	8	0	-2.153721	-1.502546	0.109459
10	1	0	-2.953581	-0.987914	-0.087969
11	1	0	2.290613	-2.019937	0.393628
12	1	0	-0.905597	2.717416	0.833424
13	1	0	1.968082	1.172578	-0.645067
14	1	0	-0.192936	2.087731	-1.276418

IM3 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.201537	-0.037377	0.001783
2	7	0	-0.304543	-1.187045	-0.074923
3	7	0	-0.507853	1.202282	-0.023718
4	6	0	1.022955	-1.034214	-0.012143
5	6	0	0.787267	1.190417	0.001219
6	7	0	1.639556	0.120457	0.035900
7	8	0	1.713686	-2.175407	-0.007171
8	8	0	-2.071526	-0.184496	-1.100454
9	8	0	1.447203	2.366242	-0.011046

10	1	0	0.786321	3.077960	-0.026885
11	1	0	2.661486	-1.959101	0.018629
12	1	0	-2.629152	0.609198	-1.134773
13	1	0	-0.699482	-2.118846	-0.118440
14	8	0	-1.953266	-0.072653	1.199912
15	1	0	-2.650189	-0.741518	1.105576

IM4 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.114309	1.463473	0.379489
2	7	0	-1.170412	0.542385	0.613305
3	7	0	1.274019	0.707550	0.262148
4	6	0	-1.069563	-0.670677	-0.252440
5	6	0	1.180060	-0.591379	0.009773
6	7	0	0.092707	-1.338743	-0.194821
7	8	0	-2.244077	-1.377779	-0.139225
8	8	0	-0.212022	2.272179	-0.715193
9	8	0	2.346994	-1.273253	-0.047557
10	1	0	3.046985	-0.630737	0.146890
11	1	0	-2.013935	-2.312646	-0.268810
12	1	0	0.240096	1.903548	-1.489861
13	1	0	-1.998931	1.087359	0.366671
14	1	0	0.112920	2.113532	1.261945
15	1	0	-1.237335	0.282930	1.613605

IM5 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.764415	1.192657	0.024874
2	7	0	0.534518	1.206025	0.052823
3	7	0	-1.569587	0.089842	0.001760
4	6	0	1.185788	-0.079094	-0.001240
5	6	0	-0.921250	-1.094158	-0.029642
6	7	0	0.378276	-1.276381	-0.070465
7	8	0	1.987498	-0.118880	-1.154625
8	1	0	2.358362	0.769885	-1.282891
9	8	0	1.949202	-0.159227	1.177827

10	8	0	-1.454899	2.341288	0.027746
11	8	0	-1.679548	-2.199384	-0.034085
12	1	0	-2.616079	-1.940684	-0.013941
13	1	0	2.263112	-1.075125	1.260773
14	1	0	-0.826610	3.082711	0.048376

IM6 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.726364	-0.448223	0.107542
2	7	0	-1.126060	0.767631	-0.298474
3	7	0	-1.184448	-1.096027	1.160514
4	6	0	0.057933	1.392182	0.027020
5	6	0	1.673857	-0.546381	-0.122506
6	7	0	1.127351	0.586758	0.472702
7	8	0	0.187147	2.606480	-0.041583
8	8	0	-2.725764	-0.834126	-0.498320
9	8	0	2.726034	-1.029584	0.254349
10	1	0	1.812153	1.109657	1.008574
11	1	0	-0.483374	-0.684685	1.758398
12	1	0	-1.758341	1.350664	-0.835339
13	8	0	0.933393	-1.020005	-1.133393
14	1	0	1.367064	-1.820809	-1.473856
15	1	0	-1.654432	-1.930948	1.478264

IM7 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.568381	-0.413980	-0.331130
2	7	0	-0.948685	0.785465	-0.696877
3	7	0	-1.300735	-0.908139	0.930308
4	6	0	0.196198	1.415136	-0.240122
5	6	0	1.740526	-0.597983	-0.110379
6	7	0	1.217249	0.620579	0.307701
7	8	0	0.331803	2.627273	-0.312153
8	8	0	-2.310957	-1.003877	-1.106843
9	8	0	2.730925	-1.082527	0.406641
10	1	0	1.873900	1.156881	0.864905

11	1	0	-1.947445	-1.643214	1.202602
12	1	0	-1.459351	1.313429	-1.395770
13	8	0	1.064105	-1.147849	-1.127417
14	1	0	1.478620	-2.002445	-1.335378
15	8	0	-1.149696	0.031738	1.969765
16	1	0	-0.260026	-0.127095	2.325559

IM8 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.492169	-0.576887	-0.177353
2	7	0	-1.029049	0.755895	-0.473789
3	7	0	-1.931344	-0.589277	1.395013
4	6	0	0.123676	1.354039	-0.080886
5	6	0	1.740955	-0.580135	0.043657
6	7	0	1.082144	0.518494	0.564496
7	8	0	0.336123	2.560475	-0.187013
8	8	0	-2.377928	-1.074394	-0.916751
9	8	0	2.655091	-1.137676	0.631548
10	1	0	1.638413	1.013989	1.252410
11	1	0	-1.161101	-0.332604	2.015188
12	1	0	-1.653495	1.349856	-1.016467
13	8	0	1.292685	-0.943985	-1.168326
14	1	0	1.785826	-1.736082	-1.440101
15	1	0	-2.218718	-1.542699	1.619394
16	1	0	-2.725725	0.034304	1.581354

TS1-1 (only one imaginary Frequencies -1407.6585)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.203594	-0.033488	0.029673
2	7	0	0.287264	-1.152583	-0.438124
3	7	0	0.560203	1.222529	-0.075430
4	6	0	-1.014955	-1.001040	-0.023262
5	6	0	-0.744152	1.229821	-0.009803
6	7	0	-1.596735	0.173371	0.085673
7	8	0	-1.711885	-2.143007	0.009106
8	8	0	1.525295	-0.417063	1.341134

9	8	0	-1.382354	2.416130	-0.028155
10	1	0	-0.710092	3.115807	-0.075034
11	1	0	-2.648920	-1.931012	0.160623
12	1	0	2.104759	0.268577	1.711015
13	1	0	0.678304	-2.075948	-0.249684
14	8	0	2.370914	-0.067272	-0.722897
15	1	0	2.277639	0.568827	-1.449622
16	1	0	0.460501	-1.131525	-1.875286

TS7-1 (only one imaginary Frequencies -1347.8482)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.684264	-0.404031	-0.044847
2	7	0	-1.075476	0.834291	-0.345286
3	7	0	-1.431735	-0.914943	1.232736
4	6	0	0.133483	1.379946	0.004521
5	6	0	1.704074	-0.591823	-0.086788
6	7	0	1.115561	0.502315	0.545007
7	8	0	0.364621	2.576977	-0.095949
8	8	0	-2.634460	-0.809010	-0.725636
9	8	0	2.759219	-1.069716	0.286310
10	1	0	1.783161	0.998739	1.127019
11	1	0	-0.518316	-0.702167	1.631604
12	1	0	-1.648567	1.438937	-0.926000
13	8	0	0.973129	-1.051516	-1.112447
14	1	0	1.427298	-1.826418	-1.485103
15	1	0	-1.643068	-1.908778	1.291119
16	1	0	-2.278792	-0.430376	2.278622

CA1 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.278023	-0.172094	-0.000332
2	7	0	0.523502	-1.273546	-0.000102
3	7	0	0.841406	1.090214	-0.000256
4	6	0	-0.787914	-1.020691	-0.000162
5	6	0	-0.489810	1.192792	-0.000279
6	7	0	-1.364681	0.183550	-0.000118

7	8	0	-1.626515	-2.057230	0.000434
8	1	0	-1.107625	-2.879678	0.000626
9	8	0	2.595099	-0.379818	0.000271
10	1	0	3.046932	0.481173	0.000403
11	8	0	-0.968871	2.437061	0.000124
12	1	0	-1.940391	2.396824	0.000302

CA2 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.001765	1.426458	-0.000050
2	7	0	-1.160523	0.671849	0.000128
3	7	0	1.161933	0.668790	0.000048
4	6	0	-1.236483	-0.711594	0.000073
5	6	0	1.234653	-0.714819	0.000482
6	7	0	-0.001647	-1.340763	0.000054
7	8	0	-2.293472	-1.320683	-0.000176
8	8	0	0.003107	2.646384	-0.000120
9	8	0	2.290635	-1.325636	-0.000282
10	1	0	-0.002966	-2.354163	-0.000057
11	1	0	2.040301	1.174283	-0.000087
12	1	0	-2.037452	1.179950	0.000130

R1 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.265441	-0.245551	-0.051693
2	7	0	0.903936	1.040142	-0.048767
3	7	0	0.447365	-1.300419	-0.054415
4	6	0	-0.418695	1.221032	-0.048435
5	6	0	-0.846868	-0.970761	-0.053975
6	7	0	-1.351493	0.265060	-0.051498
7	8	0	-0.823676	2.491323	-0.043049
8	8	0	2.567989	-0.530440	-0.052249
9	8	0	-1.744768	-1.956538	-0.054627
10	1	0	-1.273699	-2.807115	-0.056120
11	1	0	-1.795723	2.507084	-0.043427
12	1	0	3.069308	0.302595	-0.050005

13	1	0	0.005838	-0.099130	3.356325

R2 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.445462	-0.966249	0.019072
2	7	0	-0.885569	0.303920	0.028072
3	7	0	0.841325	-1.323945	0.007743
4	6	0	0.063160	1.241286	0.005975
5	6	0	1.691135	-0.293510	-0.005774
6	7	0	1.375373	1.006057	-0.010322
7	8	0	-3.182198	-0.058518	-0.134158
8	1	0	-3.245663	0.432611	0.707402
9	8	0	-0.364864	2.499625	0.004177
10	8	0	-1.350280	-1.923261	0.023879
11	8	0	2.995821	-0.559559	-0.017971
12	1	0	3.119012	-1.524220	-0.015094
13	1	0	0.405467	3.093489	-0.008506
14	1	0	-2.237542	-1.459575	0.014703

R3 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.051921	0.718220	1.235551
2	7	0	-0.051921	-0.665552	1.161288
3	7	0	-0.052848	1.345718	0.000000
4	6	0	-0.050071	-1.421816	0.000000
5	6	0	-0.051921	0.718220	-1.235551
6	7	0	-0.051921	-0.665552	-1.161288
7	8	0	-0.047892	-2.641807	0.000000
8	8	0	-0.051407	1.328496	2.291982
9	8	0	-0.051407	1.328496	-2.291982
10	1	0	-0.049585	-1.172183	-2.039176
11	1	0	-0.052460	2.359184	0.000000
12	1	0	-0.049585	-1.172183	2.039176
13	1	0	3.377582	-0.326328	0.000000

R4 (without imaginary frequency)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.817773	1.411555	-0.000463
2	7	0	-1.848470	0.486527	0.001963
3	7	0	0.449152	0.840676	-0.003808
4	6	0	-1.710191	-0.891940	0.001940
5	6	0	0.725757	-0.510654	-0.004450
6	7	0	-0.389728	-1.321599	-0.001411
7	8	0	-2.656601	-1.659293	0.004523
8	8	0	-0.999916	2.616208	0.000170
9	8	0	1.864796	-0.966508	-0.007471
10	1	0	-0.232022	-2.323257	-0.001679
11	1	0	1.235186	1.481019	-0.005905
12	1	0	-2.793671	0.853154	0.004502
13	8	0	4.489241	0.031499	0.008636
14	1	0	3.546912	-0.279160	-0.003156

HIGHEST OCCUPIED MOLECULAR ORBITALS

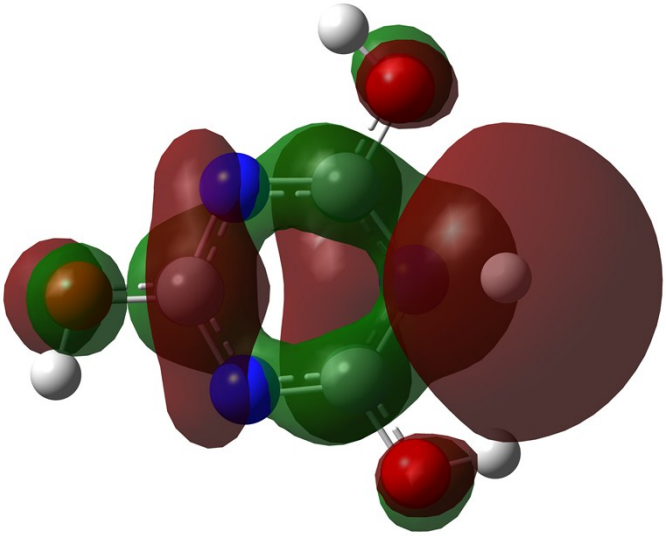

Figure S2. (a) HOMO of TS1. The electron density is plotted for iso-values of 0.003 au with the red and green denoting opposite signs.

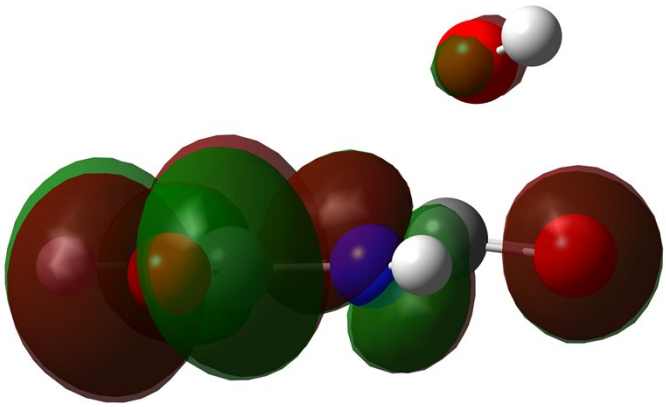

Figure S2. (b) HOMO of TS7. The electron density is plotted for iso-values of 0.003 au with the red and green denoting opposite signs.

Molecular orbital is an intuitive way to show the electron distribution and molecular interaction. Here, the highest occupied molecular orbitals (HOMOs) of •H with CA1 molecule and •OH with CA2 molecule are plotted in Figure S2. Analysis of the HOMO is performed to help understanding the interaction between the radicals and CA. Comparing with the HOMO of TS7, the electron distribution of s-triazine ring structure are modified in TS1 and there is a clearly coupling of the lone pair electrons of nitrogen atoms and hydrogen radical. The delocalized π electron of s-triazine ring structure induced by•H is a significant sign for strong interaction when •H add to CA1 molecule.

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