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Supporting Information

Reaction mechanism and kinetics of the degradation of bromoxynil initiated by OH radical

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Table S1: Relative energy (ΔE in kcal/mol), enthalpy of reaction (ΔH in kcal/mol) and Gibb's free energy (ΔG in kcal/mol) of the reactive species involved in the initial oxidation reaction of bromoxynil by OH radical

Reactive Species	B3LYP/6-311++G(d,p)			MPW1K/6-311++G(d,p)		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
R	0.0	0.0	0.0	0.0	0.0	0.0
TS1	2.76	2.55	3.01	1.35	1.52	2.3
I1	-23.13	-23.32	-24.93	-19.03	-18.87	-19.17
TS2	6.51	5.13	6.27	5.7	6.22	9.25
I2	-14.8	-12.86	-10.68	-18.5	-16.0	-12.57
TS3	11.15	6.93	7.6	8.06	5.31	7.88
I3	-0.65	-1.05	-4.04	-0.37	-0.01	-1.36
TS4	58.7	56.23	56.6	54.78	55.12	55.57
I4	-81.57	-78.76	-76.27	-98.85	-96.17	-94.82
TS5	*	*	*	*	*	*
I5	-30.54	-30.8	-32.76	-25.5	-21.17	-23.33
TS6	*	*	*	*	*	*
I6	*	*	*	*	*	*

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Table S2: Relative energy (ΔE in kcal/mol), enthalpy of reaction (ΔH in kcal/mol) and Gibb's free energy (ΔG in kcal/mol) of the reactive species involved in the subsequent reaction of the intermediate, I1.

Reactive Species	B3LYP/6-311++G(d,p)			MPW1K/6-311++G(d,p)		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
I1+O_2	0.0	0.0	0.0	0.0	0.0	0.0
TS7	13.97	15.83	23.36	11.13	11.93	14.23
I7	-3.4	-5.47	-12.34	-0.8	-0.75	-0.72
I7+HO_2	0.0	0.0	0.0	0.0	0.0	0.0
TS8	57.6	57.22	59.61	52.01	51.02	51.25
P1	0.26	0.06	0.42	4.5	3.48	0.18
I7+NO	0.0	0.0	0.0	0.0	0.0	0.0
TS9	10.31	10.56	9.87	8.5	8.37	8.12
I8	3.05	2.65	2.44	2.08	1.96	6.38
I1+O_2	0.0	0.0	0.0	0.0	0.0	0.0
TS10	20.38	22.25	29.58	5.91	4.1	11.91
I9	-23.23	-24.28	-28.57	-29.5	-30.82	-25.42
I9	0.0	0.0	0.0	0.0	0.0	0.0
TS11	20.26	21.56	28.33	13.55	14.82	15.71
P2	-21.36	-24.7	-24.3	-17.3	-18.03	-19.73
I1+O_2	0.0	0.0	0.0	0.0	0.0	0.0
TS12	20.4	22.24	29.57	29.72	32.18	41.02
I10	-1.79	-4.21	-10.6	-3.38	-0.35	-7.33
TS13	*	*	*	17.65	19.68	28.39
I11	-3.4	-4.32	-4.01	-7.47	-4.09	-3.38

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Table S3: Relative energy (ΔE in kcal/mol), enthalpy of reaction (ΔH in kcal/mol) and Gibb's free energy (ΔG in kcal/mol) of the reactive species involved in the subsequent reaction of the intermediate, I2.

Reactive Species	B3LYP/6-311++G(d,p)			MPW1K/6-311++G(d,p)		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
I2+I2	0.0	0.0	0.0	0.0	0.0	0.0
TS14	3.68	4.33	3.77	1.88	1.43	2.77
I12	-17.51	-16.22	-14.92	-25.68	-21.65	-22.8
TS15	16.57	15.11	15.43	14.23	14.96	13.75
P3	-77.94	-75.67	-73.32	-90.2	-88.0	-85.78
I2+I2	0.0	0.0	0.0	0.0	0.0	0.0
I13	-14.41	-12.03	-12.14	-13.68	-14.01	-13.9
TS16	8.15	8.73	9.11	6.92	7.01	7.52
I14	-91.2	-89.76	-83.27	-87.13	-80.1	-79.52
TS17	*	*	*	*	*	*
P4	*	*	*	*	*	*
I2+NO_2	0.0	0.0	0.0	0.0	0.0	0.0
TS18	13.85	12.01	7.42	21.24	19.55	22.06
P5	2.7	4.3	7.2	3.27	2.24	2.4

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Table S4: Relative energy (ΔE in kcal/mol), enthalpy of reaction (ΔH in kcal/mol) and Gibb's free energy (ΔG in kcal/mol) of the reactive species involved in the subsequent reaction of the intermediate, I3.

Reactive Species	B3LYP/6-311++G(d,p)			MPW1K/6-311++G(d,p)		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
I3+O_2	0.0	0.0	0.0	0.0	0.0	0.0
I15	1.18	1.12	1.08	0.8	0.75	0.72
I15+HO_2	0.0	0.0	0.0	0.0	0.0	0.0
TS19	6.06	5.4	5.5	12.01	11.02	11.25
P6	-14.27	-7.89	-2.73	-12.5	-10.48	-3.8
I15+NO	0.0	0.0	0.0	0.0	0.0	0.0
TS20	24.97	23.6	25.96	31.55	30.54	31.57
I16	-33.54	-31.81	-30.8	-37.54	-35.75	-34.93
I15+NO_2	0.0	0.0	0.0	0.0	0.0	0.0
TS21	9.72	10.37	12.74	16.8	16.21	17.62
P7	-23.28	-20.97	-18.5	-28.4	-26.64	-25.63
I15+I15	0.0	0.0	0.0	0.0	0.0	0.0
TS22	*	*	*	*	*	*
P8	-9.28	-9.67	-12.32	-14.23	-15.1	-17.9

***Structure not converged**

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Table S5: The rate constant, k_{I1}, k_{I2} and k_{I3}($cm^3molecule^{-1}s^{-1}$) calculated for the formation of intermediates, I1, I2 and I3 over the temperature range of 278-350K

Temperature (K)	k_{I1} ($x10^{-22}$)			k_{I2} ($x10^{-11}$)			k_{I3} ($x10^{-20}$)		
	TST	TST/SCT	CVT	TST	TST/SCT	CVT	TST	TST/SCT	CVT
278	6.52	9.61	5.48	0.03	0.08	0.003	0.06	0.09	0.06
288	7.12	10.22	5.96	0.24	0.51	0.02	0.14	0.16	0.13
298	7.74	10.86	6.45	1.54	2.67	0.13	0.32	0.40	0.32
308	8.37	11.57	6.94	8.17	12.81	0.78	0.61	0.80	0.58
318	9.01	12.15	7.45	40.18	55.83	4.13	1.18	1.52	1.13
328	9.67	12.82	7.96	179.07	223.77	19.61	2.22	2.77	2.12
338	10.34	13.55	8.48	730.22	830.54	84.68	4.01	4.93	3.84
348	11.03	14.18	9.01	2745.7	2872.7	336.11	7.01	8.37	6.72
350	11.17	14.32	9.11	3546.0	3652.7	438.61	7.81	9.28	7.48

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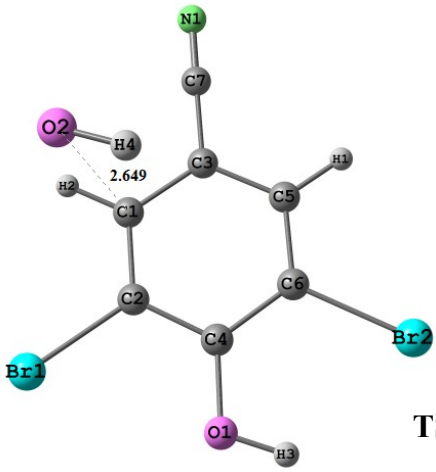

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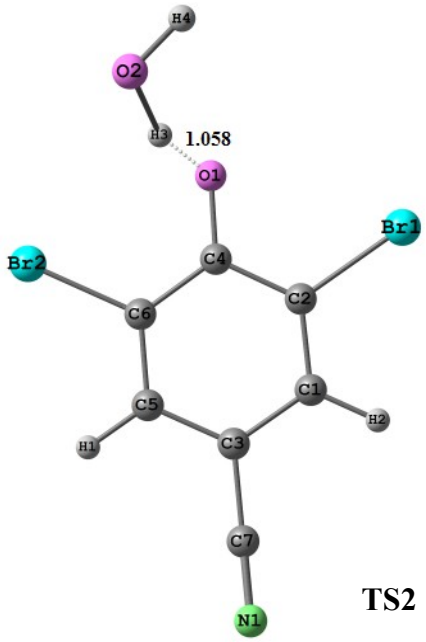

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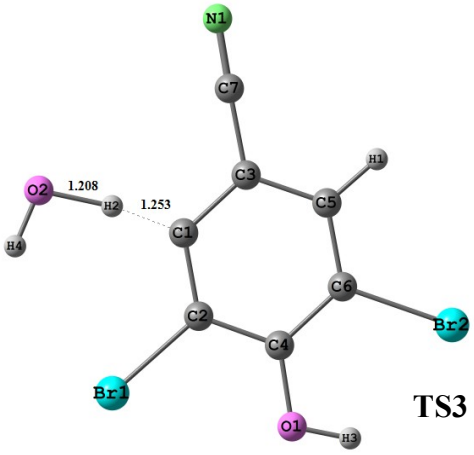

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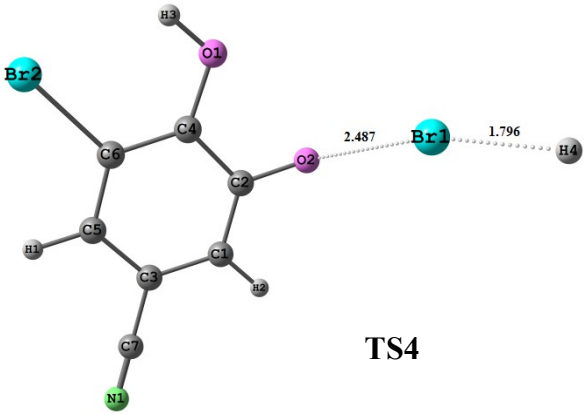

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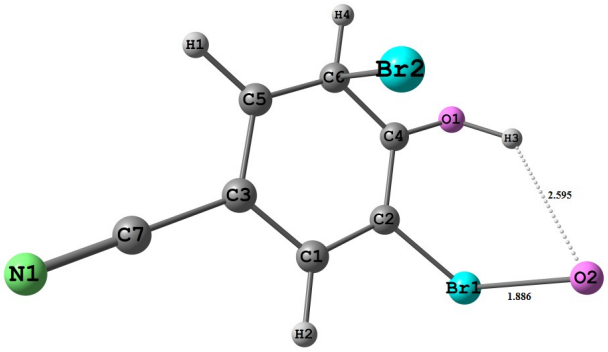

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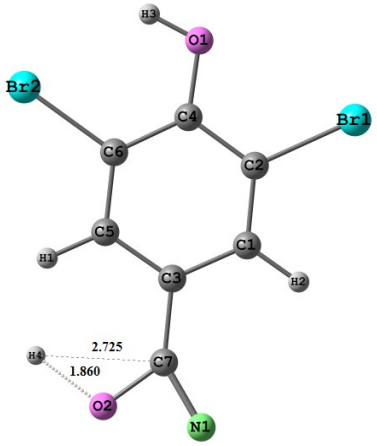

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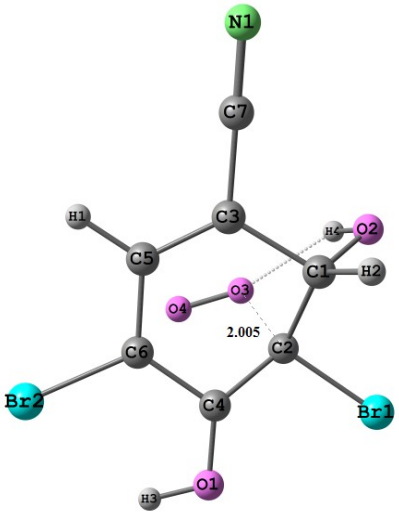

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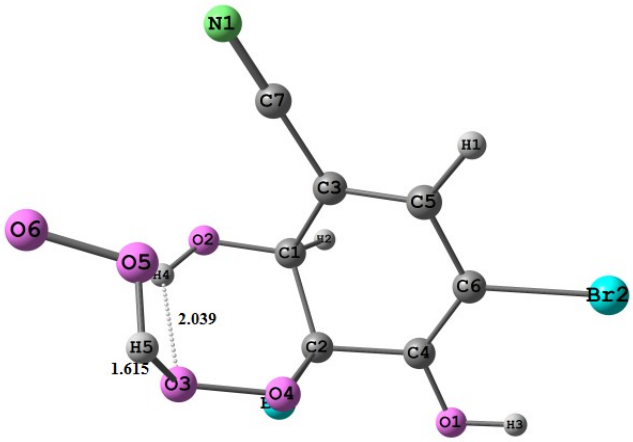

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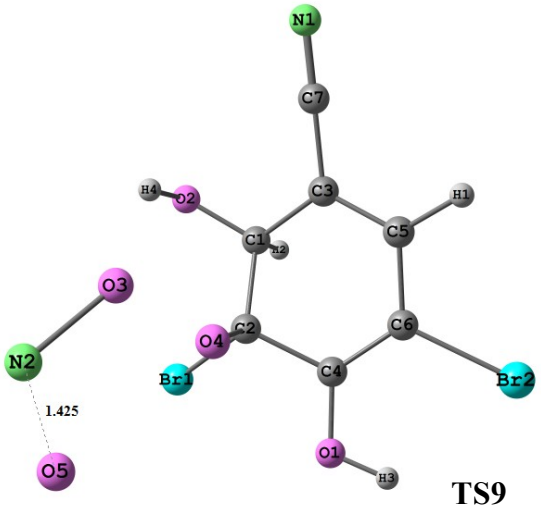

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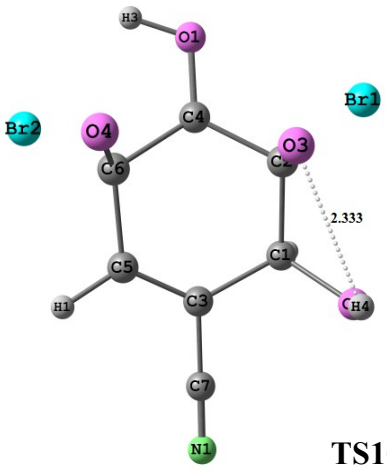

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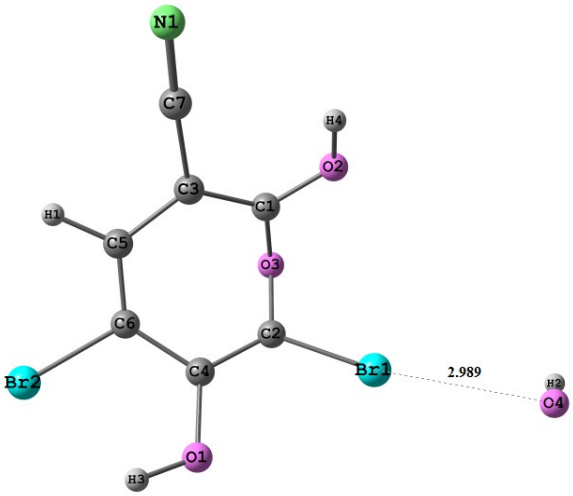

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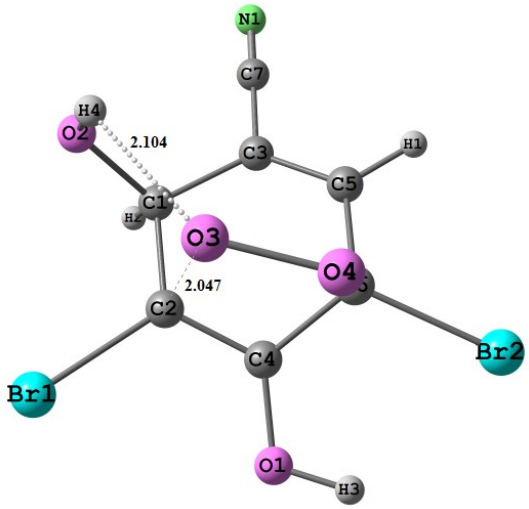

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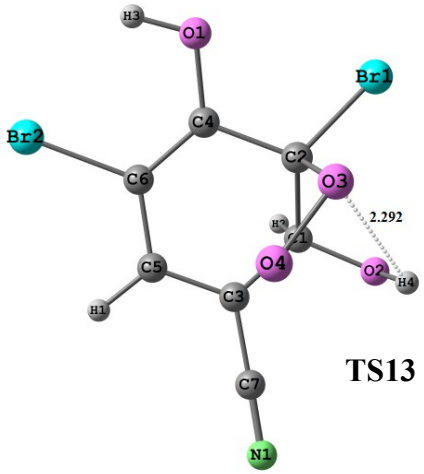

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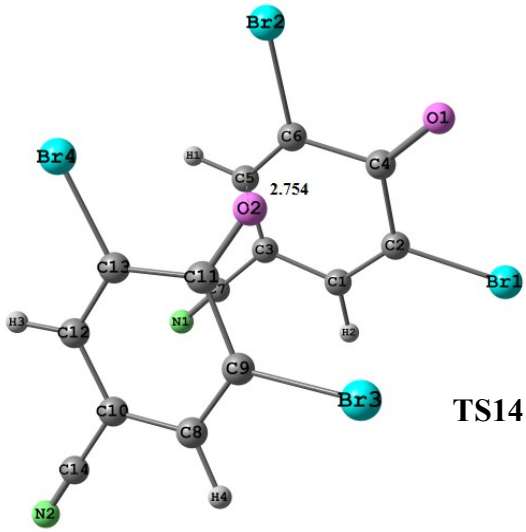

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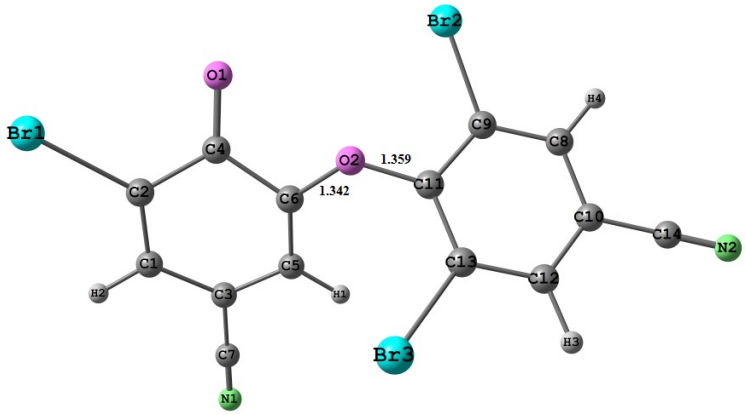

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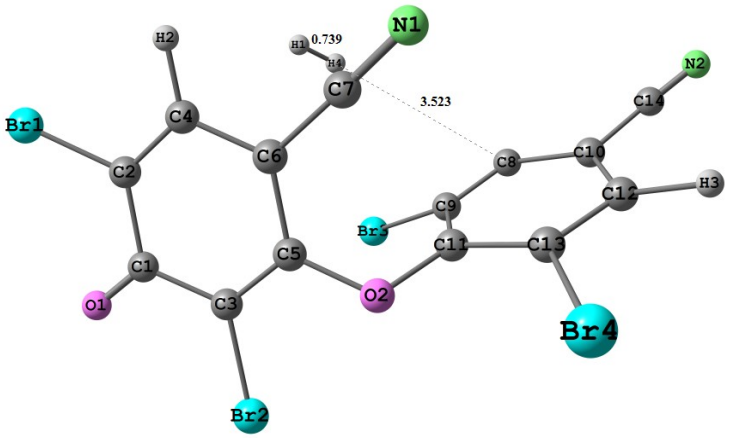

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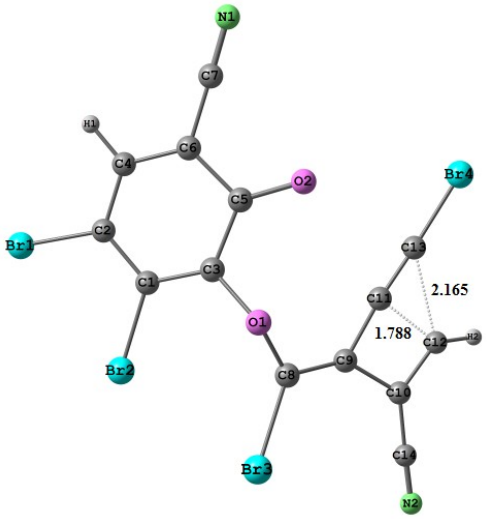

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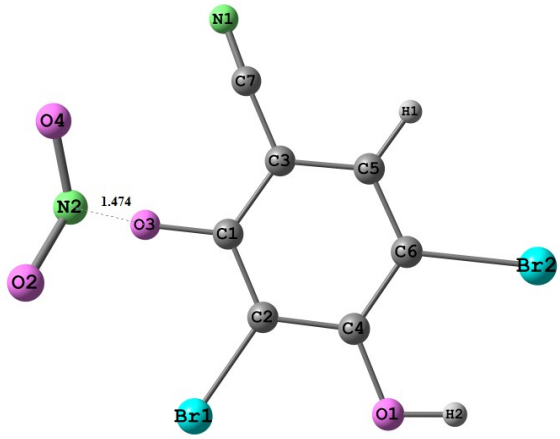

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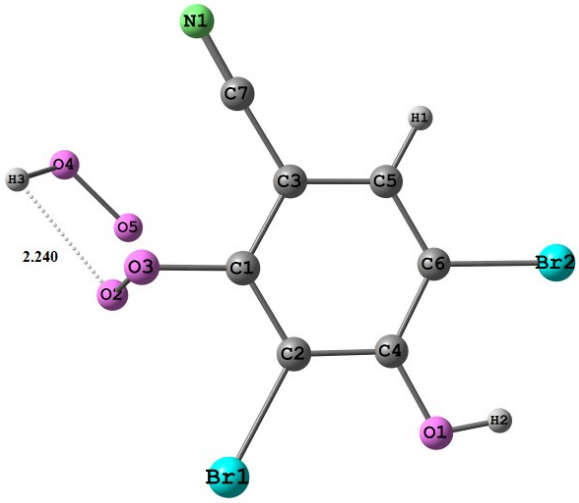

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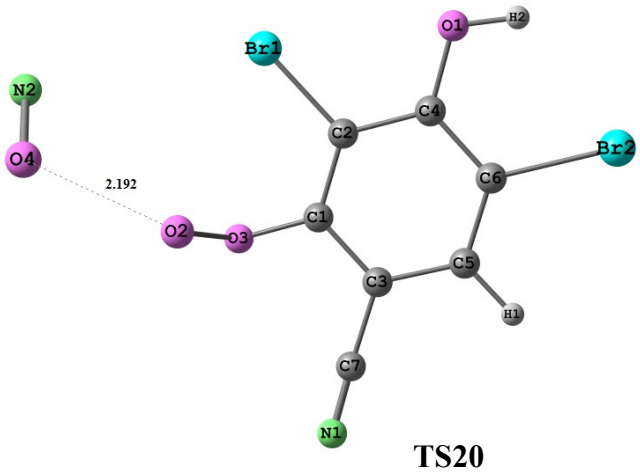

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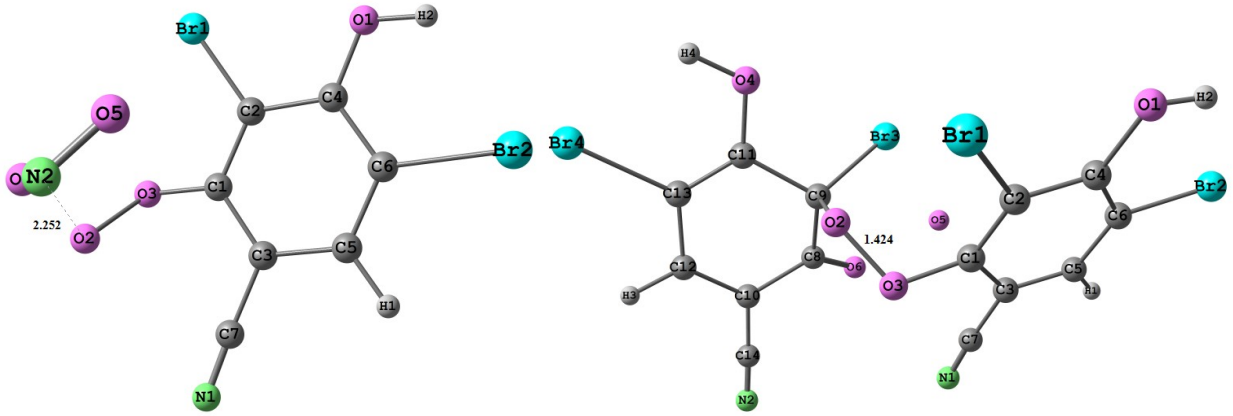

TS21 **TS22**

Figure S1: The optimized structure of the transition states corresponding to the OH initiated and subsequent reactions of bromoxynil

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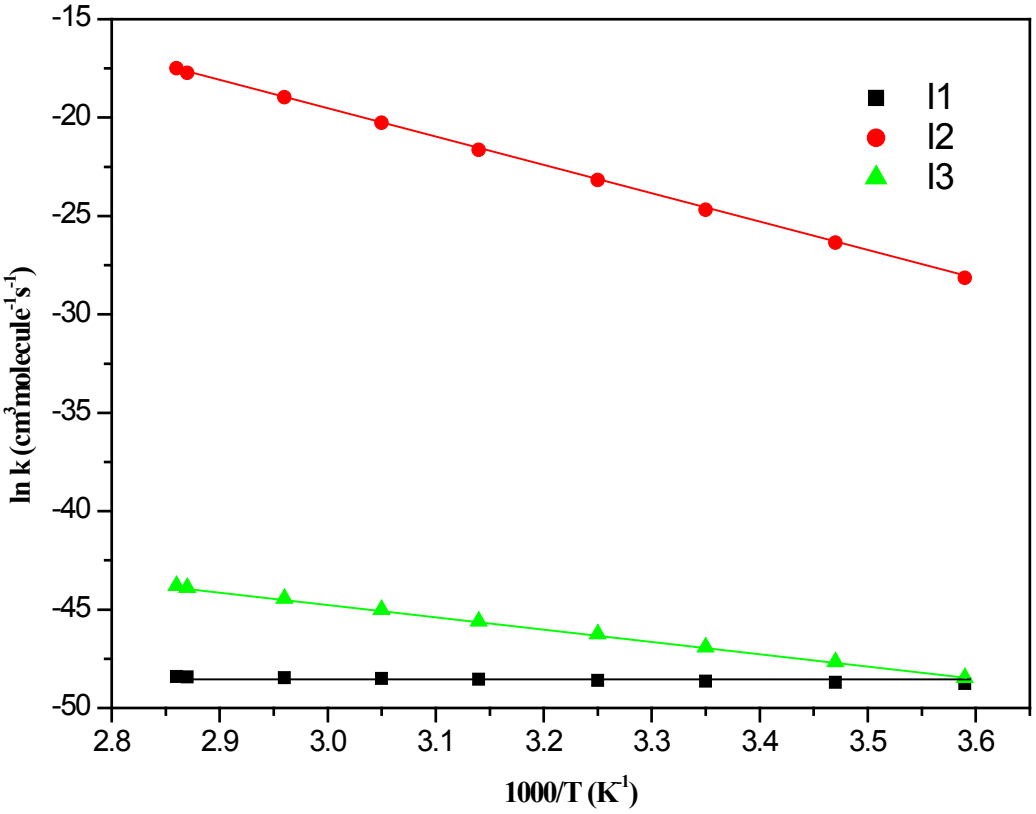

Figure S2: Arrhenius plot of the rate constant calculated for the intermediates, I1, I2 and I3 over the temperature range of 278-350 K