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Supporting information

Dehydro-oxazole, thiazole and imidazole radicals: Insights into the electronic structure, stability and reactivity aspects

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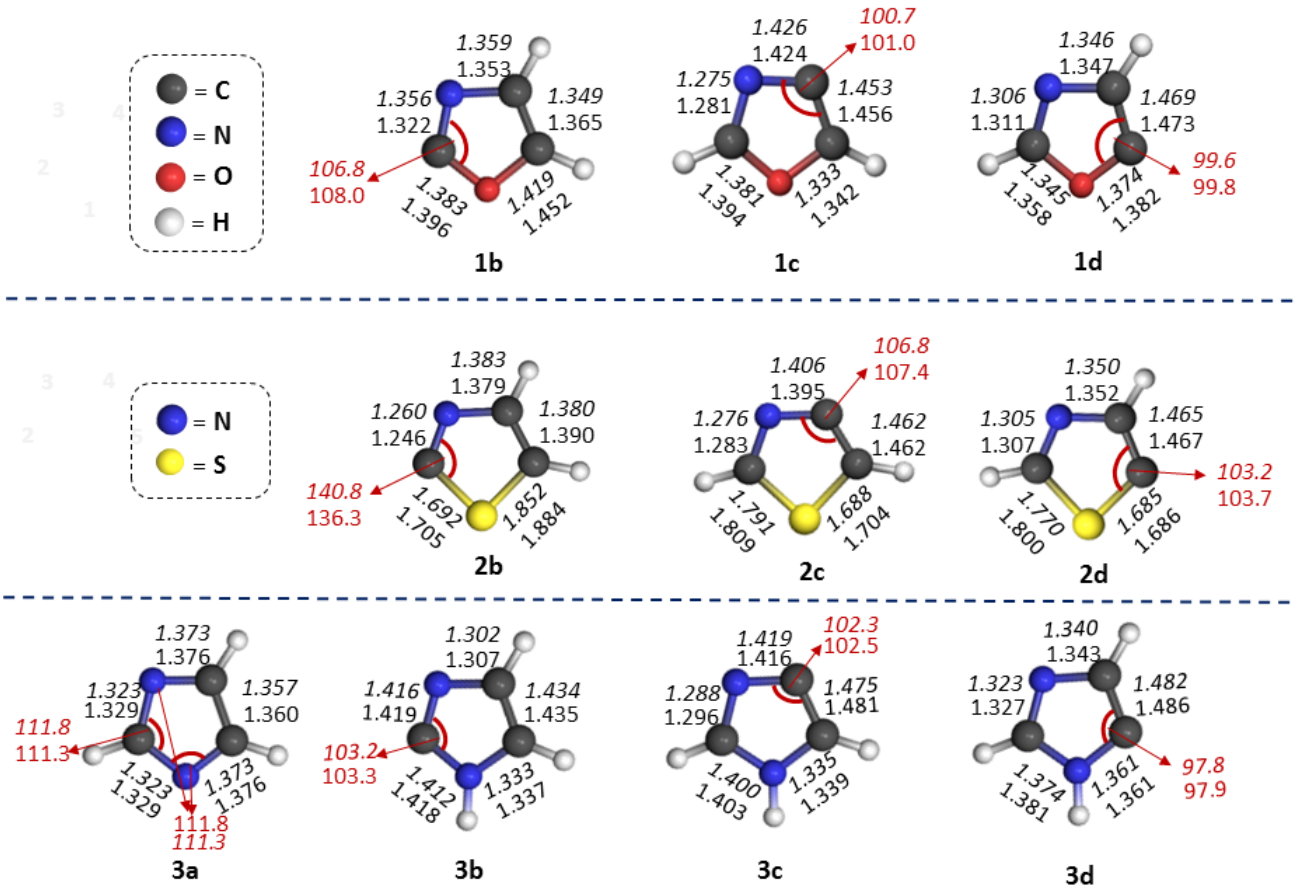


Fig 1S: The important geometrical parameters of $^2A''$ symmetric structure of all the carbon radicals and $^2A'$ symmetry in case of **3a.** The normal font indicate (U)B3LYP/cc-pVTZ and italics indicate (U)M06-2X/cc-pVTZ level of theory

Table 1S: The energy difference between $^2A'$ and $^2A''$ structures of all the radical isomers at (U)B3LYP/cc-pVTZ, (U)M06-2X/cc-pVTZ and (U)CCSD(T)/cc-pVTZ levels of theory.

Species	Radical isomer	Level of theory	$^2A'$		$^2A''$		ΔE ($^2A''$-$^2A'$) kcal/mol
			Energy (Hartrees)	Number of Imaginary frequencies	Energy (Hartrees)	Number of imaginary frequency	
		***C*-centred Radicals**					
oxazole	1b	UB3LYP/cc-pVTZ	–245.41625	0	–245.21205	1	128.1
		(U)M06-2X/cc-pVTZ	–245.32472	0	–245.12038	1	128.2
		CCSD(T)/cc-pVTZ*	–244.93070	NA	–244.90336	NA	17.1
	1c	UB3LYP/cc-pVTZ	–245.41706	0	–245.36482	0	32.8
		(U)M06-2X/cc-pVTZ	–245.32487	0	–245.31543	0	5.9
		CCSD(T)/cc-pVTZ*	–244.93033	NA	–244.90766	NA	14.2
	1d	UB3LYP/cc-pVTZ	–245.41247	0	–245.38870	0	14.9
		(U)M06-2X/cc-pVTZ	–245.32099	0	–245.29355	0	17.2
		CCSD(T)/cc-pVTZ*	–244.92704	NA	–244.90404	NA	14.4
Thiazole	2b	UB3LYP/cc-pVTZ	–568.41653	0	–568.30790	1	68.2
		(U)M06-2X/cc-pVTZ	–568.31488	0	–568.16645	1	93.1
		CCSD(T)/cc-pVTZ*	–567.56006	NA	–567.52575	NA	21.5
	2c	UB3LYP/cc-pVTZ	–568.41194	0	–568.35104	0	38.2
		(U)M06-2X/cc-pVTZ	–568.31118	0	–568.24539	0	41.3
		CCSD(T)/cc-pVTZ*	–567.55458	NA	–567.53009	NA	15.4
	2d	UB3LYP/cc-pVTZ	–568.40387	0	–568.37537	0	17.9
		(U)M06-2X/cc-pVTZ	–568.30324	0	–568.27075	0	20.4
		CCSD(T)/cc-pVTZ*	–567.54870	NA	–567.52022	NA	17.9
imidazole	3b	UB3LYP/cc-pVTZ	–225.54730	0	–225.51264	0	21.7
		(U)M06-2X/cc-pVTZ	–225.45671	0	–225.41685	0	25.0
		CCSD(T)/cc-pVTZ*	–225.09106	NA	–225.05749	NA	21.1
	3c	UB3LYP/cc-pVTZ	–225.54642	0	–225.49234	0	33.9
		(U)M06-2X/cc-pVTZ	–225.45624	0	–225.39927	0	35.7
		CCSD(T)/cc-pVTZ*	–225.08999	NA	–225.06538	NA	15.4
	3d	UB3LYP/cc-pVTZ	–225.54140	0	–225.52288	0	11.6
		(U)M06-2X/cc-pVTZ	–225.45079	0	–225.43280	0	11.3
		CCSD(T)/cc-pVTZ*	–225.08557	NA	–225.07073	NA	9.3
		***N*-centred Radicals**					
	3a (C_S)	UB3LYP/cc-pVTZ	–225.54992	1	–225.57941	0	–18.5
		(U)M06-2X/cc-pVTZ	–225.44921	1	–225.48605	0	–23.1
		CCSD(T)/cc-pVTZ*	–225.08114	NA	–225.12539	NA	–27.8
	3a(C_{2V})**	UB3LYP/cc-pVTZ	–225.39034 ($^2A_2$)	3	–225.57940 ($^2B_1$)	0	–118.6
		(U)M06-2X/cc-pVTZ	–225.28281($^2A_2$)	3	–225.48605 ($^2B_1$)	0	–127.5
		CCSD(T)/cc-pVTZ*	–225.09669 ($^2A_2$)	NA	–225.12390 ($^2B_1$)	NA	–18.0

*The single point energies have been calculated at (U)CCSD(T)/cc-pVTZ using (U)B3LYP/cc-pVTZ geometries.

** The calculations for imidazole radical **3a** with C_{2V} point group has been done seperately. A new configuration with $^2A_2$ electronic structure has been optmized and the energy difference ($^2A_2$-$^2B_1$) also been calculated.

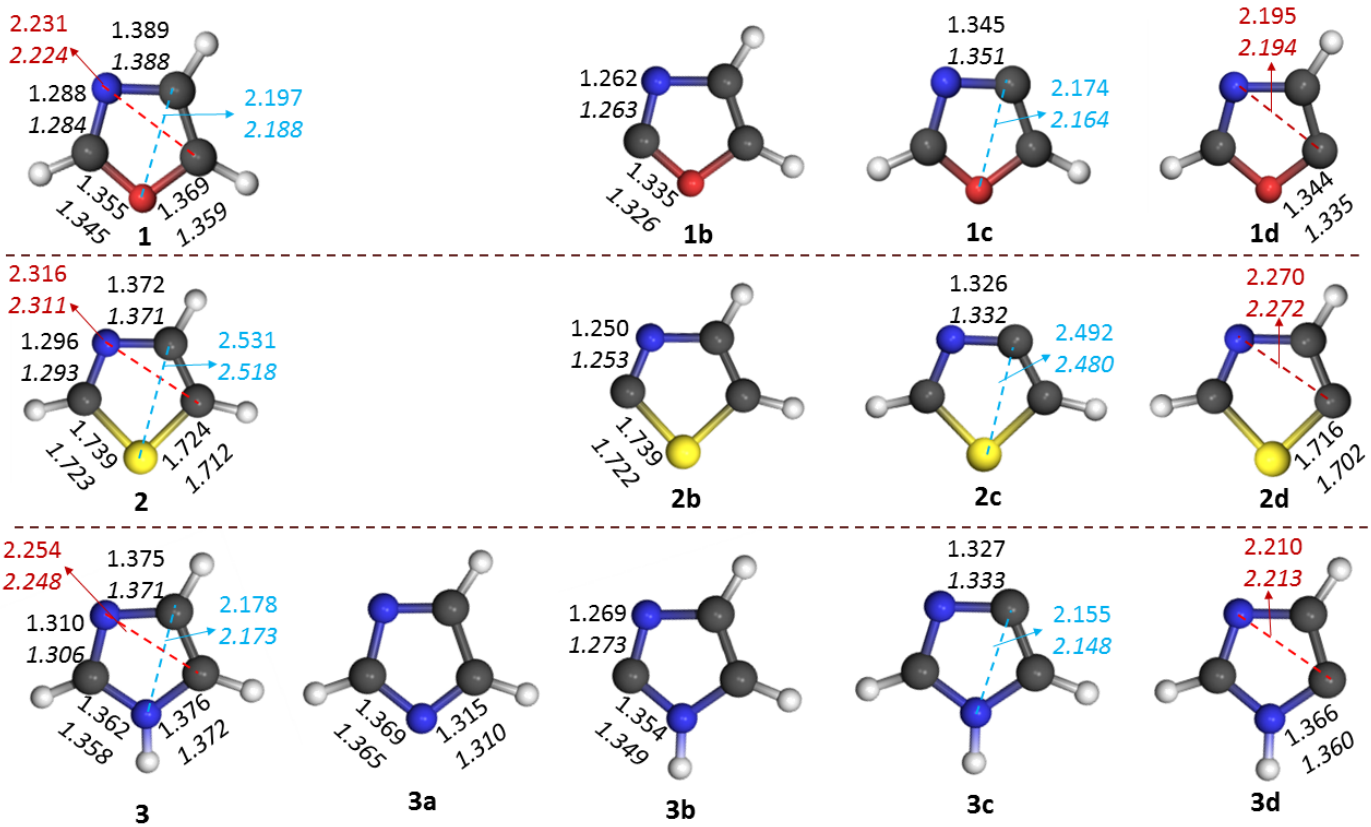


Figure 2S. Selected structural information of oxazole, thiazole, imidazole and their dehydro radicals (The bond distance between heteroatom and the radical centre in Å are indicated; The corresponding internuclear distances for the parent molecules are also separately mentioned; The values are obtained from (U)B3LYP/cc-pVTZ (normal font) and (U)M06-2X/cc-pVTZ (italics) levels of theory)

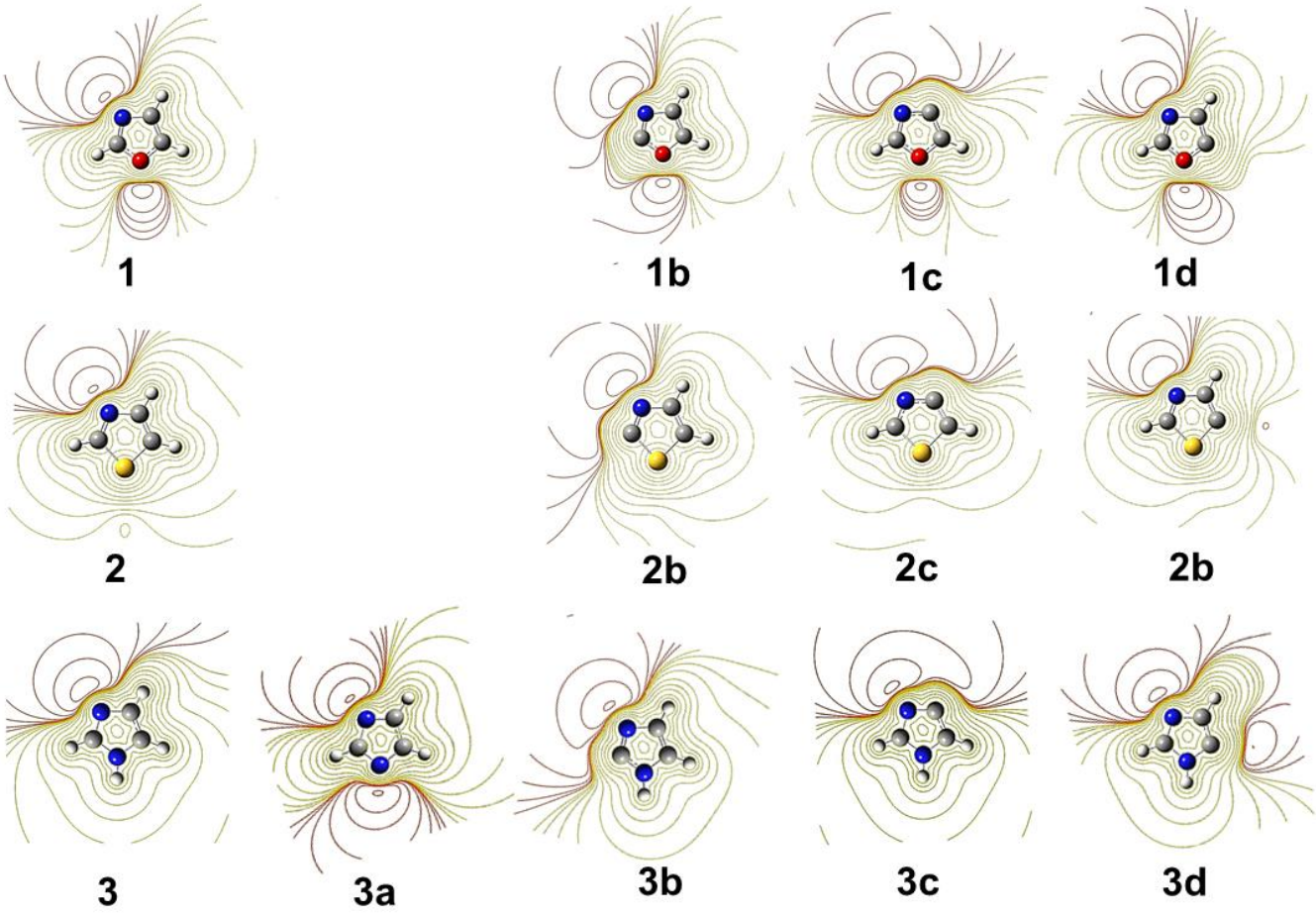
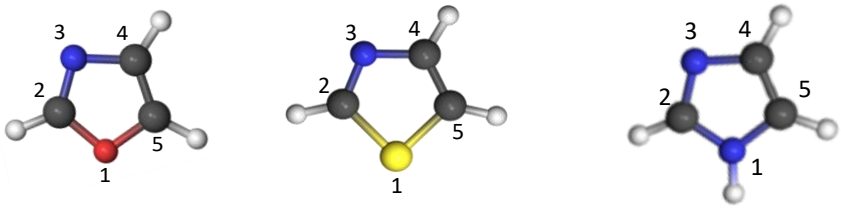


Figure 3S: Two dimensional electrostatic potential surfaces of oxazole, thiazole, imidazole and their ten isomeric radical species (The surfaces are obtained from (U)B3LYP/cc-pVTZ calculations and rendered at an isovalue of 0.002)

Table 2S. The hybridisation details of oxazole, thiazole, imidazole and their radical isomers[a]



	X_1-C_2 bond	C_2-N_3 bond	N_3-C_4 bond	C_4-C_5 bond	C_5-X_1 bond
Oxazole 1	C2: $SP^{2.66}$ (31.6%) O1: $SP^{2.40}$ (68.4%)	C2: $SP^{1.65}$ (41.9%) N3: $SP^{1.89}$ (58.0%) And C2: SP (41.7%) N3: SP(58.2%)	C4: $SP^{2.32}$ (41.9%) N3: $SP^{2.36}$ (58.1%)	C4: $SP^{1.75}$ (49.5%) C5: $SP^{1.48}$ (50.5%) and C4: SP (49.6%) C5: SP (50.4%)	C5: $SP^{3.06}$ (31.7%) O1: $SP^{2.38}$ (68.3%)
Thiazole 2	C2: $SP^{2.48}$ (49.6%) S1: $SP^{4.53}$ (50.4%)	C2: $SP^{1.72}$ (41.5%) N3: $SP^{1.77}$ (58.5%) And C2: SP (44.7%) N3: SP(55.2%)	C4: $SP^{2.22}$ (41.5%) N3: $SP^{2.17}$ (58.5%)	C4: $SP^{1.66}$ (49.2%) C5: $SP^{1.54}$ (50.8%) and C4: SP (45.6%) C5: SP (54.4%)	C5: $SP^{2.80}$ (50.8%) S1: $SP^{4.19}$ (49.2%)
Imidazole 3	C2: $SP^{2.26}$ (37.3%) N1: $SP^{1.86}$ (62.7%)	C: $SP^{1.80}$ (42.6%) N: $SP^{1.96}$ (57.4%) and C: SP (57.7%) N: SP(42.3%)	C: $SP^{2.23}$ (41.9%) N: $SP^{2.20}$ (58.1%)	C4: SP (51.4%) C5: SP (48.6%) and C4: $SP^{1.61}$ (51.4%) C5: $SP^{1.74}$ (48.6%)	C5: $SP^{2.58}$ (37.7%) N1: $SP^{1.84}$ (62.4%)
1-dh imidazole 3a	C2: $SP^{1.97}$ (59.3%) N1: $SP^{2.39}$ (40.8%)	C: $SP^{1.97}$ (59.3%) N: $SP^{2.39}$ (40.8%)	C: $SP^{1.99}$ (58.7%) N: $SP^{1.92}$ (41.3%) And C: SP (70.5%) N: SP (29.5%)	C4: $SP^{1.96}$ (50.0%) C5: $SP^{1.96}$ (50.0%)	C5: $SP^{1.99}$ (58.7%) N1: $SP^{1.92}$ (41.3%) And C5: SP (70.52%) N1: SP (29.5%
2-dh oxazole 1b	C2: $SP^{3.13}$ (29.4%) O1: $SP^{2.49}$ (70.5%)	C2: $SP^{1.63}$ (39.1%) N3: $SP^{1.94}$ (60.8%) And C2: SP (40.6%) N3: SP(59.4%)	C4: $SP^{2.37}$ (43.0%) N3: $SP^{2.60}$ (56.9%)	C4: $SP^{1.72}$ (49.7%) C5: $SP^{1.47}$ (50.3%) and C4: SP (50.1%) C5: SP (49.6%)	C5: $SP^{3.15}$ (32.3%) O1: $SP^{2.75}$ (67.7%)
2-dh thiazole 2b	C2: $SP^{3.62}$ (45.3%) S1: $SP^{4.34}$ (54.7%)	C2: $SP^{1.67}$ (38.1%) N3: $SP^{1.59}$ (61.9%) And C2: SP (41.1%) N3: SP(58.9%)	C4: $SP^{2.31}$ (42.1%) N3: $SP^{2.33}$ (57.9%)	C4: $SP^{1.65}$ (49.6%) C5: $SP^{1.51}$ (50.4%) and C4: SP (47.7%) C5: SP (52.3%)	C5: $SP^{2.84}$ (51.5%) S1: $SP^{4.88}$ (48.5%)
2-dh imidazole 3b	C2: $SP^{1.15}$ (36.9%) N1: $SP^{2.14}$ (63.1%)	C2: $SP^{1.18}$ (39.5%) N3: $SP^{1.67}$ (60.5%) And C2: SP (34.5%) N3: SP(62.5%)	C4: $SP^{2.41}$ (39.5%) N3: $SP^{2.35}$ (60.5%)	C4: $SP^{1.68}$ (48.8%) C5: $SP^{1.60}$ (51.2%) and C4: SP (48.1%) C5: SP(51.9%)	C5: $SP^{2.64}$ (36.7%) N1: $SP^{1.64}$ (63.3%)
4-dh oxazole 1c	C2: $SP^{2.62}$ (31.9%) O1: $SP^{2.35}$ (68.1%)	C2: $SP^{1.69}$ (42.5%) N3: $SP^{2.01}$ (57.5%) And C2: SP (41.0%) N3: SP(58.9%)	C4: $SP^{2.22}$ (39.2%) N3: $SP^{2.28}$ (60.8%)	C4: $SP^{1.73}$ (46.6%) C5: $SP^{1.52}$ (53.4%) and C4: SP (48.9%) C5: SP (51.1%)	C5: $SP^{3.27}$ (30.7%) O1: $SP^{2.40}$ (69.3%)

4-dh thiazole 2c	C2: $SP^{2.46}$ (50.2%) S1: $SP^{4.44}$ (49.8%)	C2: $SP^{1.74}$ (42.1%) N3: $SP^{1.94}$ (57.9%) And C2: SP (44.3%) N3: SP (55.7%)	C4: $SP^{2.09}$ (39.0%) N3: $SP^{2.08}$ (60.9%)	C4: $SP^{1.60}$ (46.4%) C5: $SP^{1.54}$ (53.6%) and C4: SP (44.9%) C5: SP (55.1%)	C5: $SP^{3.16}$ (48.1%) S1: $SP^{4.28}$ (51.9%)
4-dh imidazole 3c	C2: SP (72.4%) N1: SP(27.6%)	C2: $SP^{1.99}$ (61.2%) N3: $SP^{0.90}$ (38.8%)	C4: $SP^{1.19}$ (66.0%) N3: $SP^{1.14}$ (34.0%)	C4: $SP^{.0.85}$ (53.3%) C5: $SP^{1.78}$ (46.7%) And C4: SP (59.4%) C5: SP(40.7%)	C5: $SP^{2.37}$ (38.2%) N1: $SP^{1.88}$ (61.8%)
5-dh oxazole 1d	C2: $SP^{2.72}$ (32.2%) O1: $SP^{2.63}$ (67.8%)	C2: $SP^{1.66}$ (42.5%) N3: $SP^{1.87}$ (58.2%) And C2: SP (41.3%) N3: SP (58.7%)	C4: $SP^{2.45}$ (41.0%) N3: $SP^{2.28}$ (58.9%)	C4: $SP^{1.73}$ (46.6%) C5: $SP^{1.52}$ (53.4%) and C4: SP (48.9%) C5: SP (51.1%)	C5: $SP^{3.30}$ (29.8%) O1: $SP^{2.49}$ (70.2%)
5-dh thiazole 2d	C2: $SP^{2.50}$ (50.7%) S1: $SP^{5.04}$ (49.3%)	C2: $SP^{1.70}$ (41.3%) N3: $SP^{1.72}$ (58.7%) And C2: SP (43.3%) N3: SP (56.7%)	C4: $SP^{2.36}$ (40.6%) N3: $SP^{2.13}$ (59.4%)	C4: $SP^{1.71}$ (52.4%) C5: $SP^{1.43}$(47.6%) and C4: SP (45.4%) C5: SP (54.6%)	C5: $SP^{3.13}$ (48.7%) S1: $SP^{4.27}$ (51.3%)
5-dh imidazole 3d	C2: $SP^{2.26}$ (36.4%) N1: $SP^{1.73}$ (63.6%)	C2: $SP^{1.82}$ (42.7%) N3: $SP^{2.04}$ (57.3%) And C2: SP (43.1%) N3: SP(56.9%)	C4: $SP^{2.06}$ (43.5%) N3: $SP^{2.91}$ (56.5%)	C4: SP^{2} (51.1%) C5: $SP^{0.84}$ (48.9%) And C4: SP^{1} (56.7%) C5: SP(43.2%)	C5: $SP^{1.58}$ (35.2%) N1: $SP^{2.0}$ (64.8%)

[a]The values are obtained from NBO calculations at (U)B3LYP/cc-pVTZ level of theory; The contribution of any particular atom to corresponding bond hybridisation is given in parentheses. The numbering is indicated for the parent compounds.

Table 3S: The second order perturbation energy from the NBO analysis at (U)B3LYP/cc-pVTZ level of theory.

Species		Donor NBO	Acceptor NBO	E (2) (kcal/mol)
oxazole	1b	LP(N3)	LP*(C2)	7.0
			BD*(C2-O1)	3.9
		LP1(O1)	LP*(C2)	0.4
		LP2(O1)	BD*(C2-N3)	18.7
			BD*(C4-C5)	10.5
	1c	LP(N3)	LP*(C4)	7.17
			BD*(C4-C5)	2.2
		LP1(O1)	LP*(C4)	0.3
		LP2(O1)	BD*(C2-N3)	19.1
			BD*(C4-C5)	8.8
	1d	LP(N3)	LP*(C5)	1.1
			BD*(C4-C5)	3.0
		LP1(O1)	LP*(C5)	1.7
		LP2(O1)	BD*(C2-N3)	16.0
			BD*(C4-C5)	14.3
Thiazole	2b	LP(N3)	LP*(C2)	19.0
			BD*(C2-S1)	3.2
		LP1(S1)	LP*(C2)	2.3
		LP2(O1)	BD*(C2-N3)	13.5
			BD*(C4-C5)	9.4
	2c	LP(N3)	LP*(C4)	10.6
			BD*(C4-C5)	2.9
		LP1(O1)	LP*(C4)	0.0
		LP2(O1)	BD*(C2-N3)	16.5
			BD*(C4-C5)	6.8
	2d	LP(N3)	LP*(C5)	1.1
			BD*(C4-C5)	3.7
		LP1(O1)	LP*(C5)	0.7
		LP2(O1)	BD*(C2-N3)	13.7
			BD*(C4-C5)	11.5
Imidazole	3a	LP (N3)	BD* (N1-C2)	3.7
			BD* (C4-C5)	3.7
		LP (N1)	BD* (N3-C2)	3.8
			BD* (C4-C5)	3.6
	3b	LP (N3)	LP* (C2)	9.2
			BD* (C2-N1)	2.8
		LP (N1)	BD* (C2-N3)	22.7
			BD* (C4-C5)	14.5
	3c	LP (N3)	BD* (N1-C2)	81.0
			BD* (C4-C5)	28.9
		BD* (N1-C2)	BD* (C4-C5)	6.2
	3d	LP (N3)	LP* (C5)	1.1
			BD* (C3-C4)	3.4
		LP (N1)	BD* (C2-N3)	22.6
			BD* (C4-C5)	16.9

LP = bonding orbital of lone pair, LP* = antibonding molecular orbital of lone pair, BD* = antibonding orbital of the particular bond mentioned

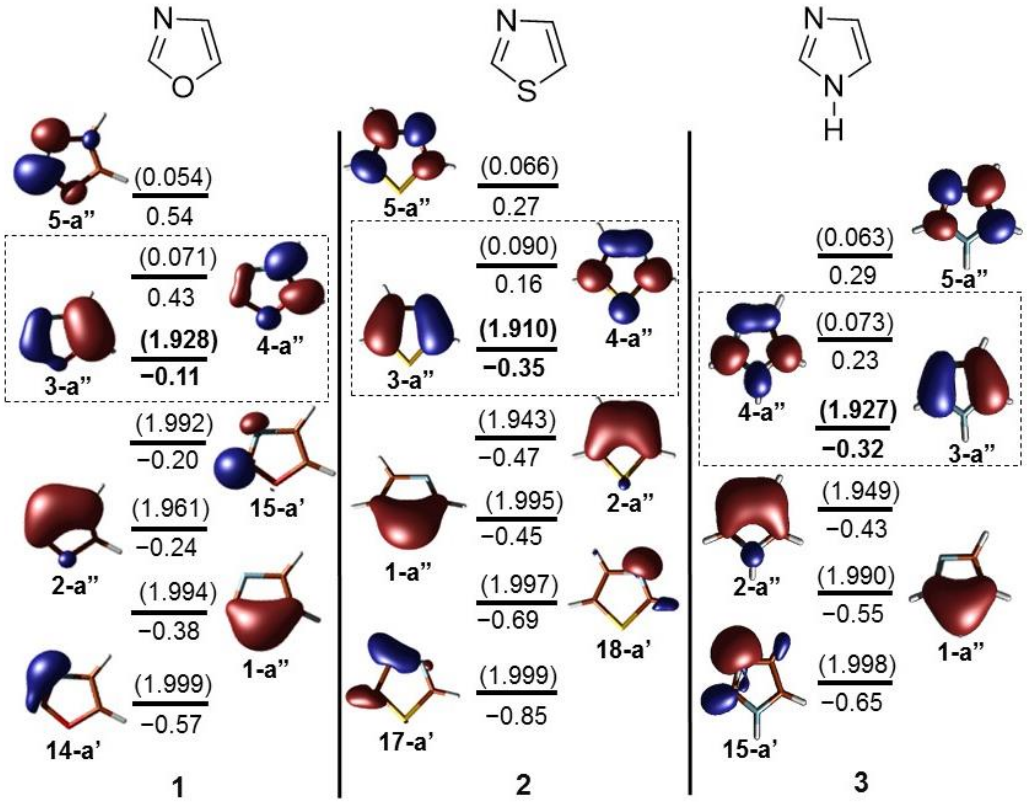


Figure 4S: Molecular orbital diagram of parent heterocyclic molecules at CASSCF/cc-pVTZ//(U)B3LYP/cc-pVTZ (The active space orbitals are indicated along with their energies in hartrees and natural orbital occupancy numbers (NOON) in parentheses; the orbital symmetries are indicated below each one of them. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have been highlighted by a box; The parameters corresponding to HOMO are indicated in bold; All the orbitals have been rendered at an isovalue 0.05)

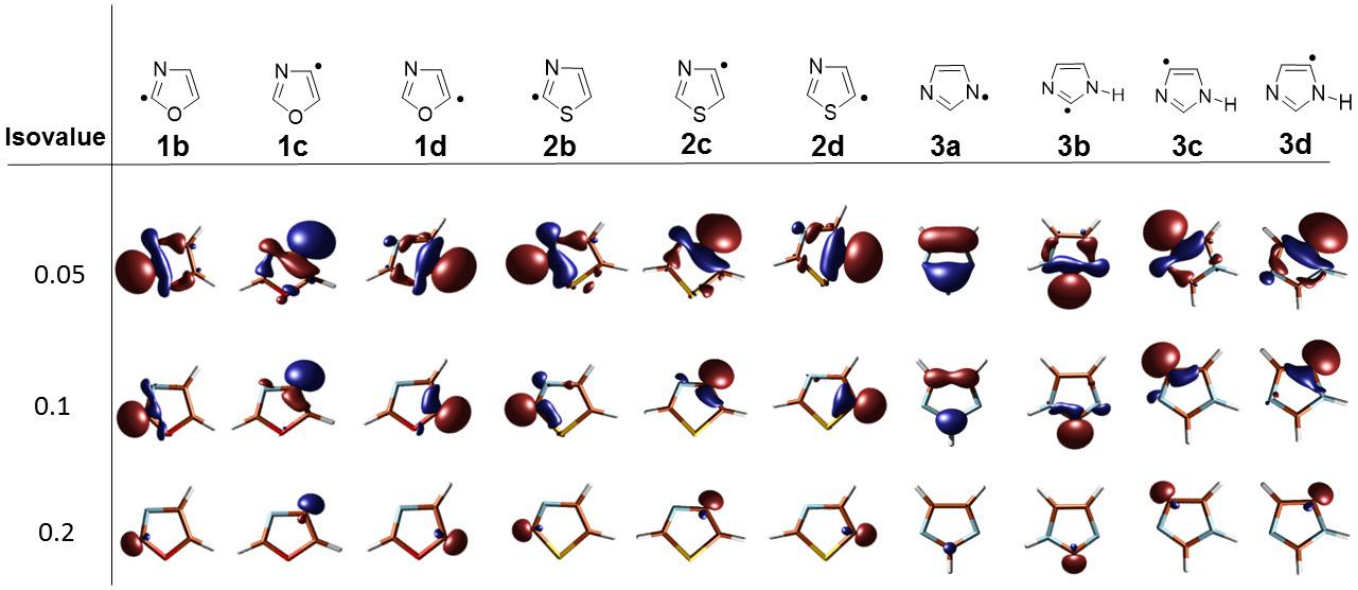


Figure 5S: Singly occupied molecular orbital's (SOMO) of dehydro- oxazole, thiazole, and imidazole radical isomers; (The SOMO's obtained at CASSCF/cc-pVTZ//(U)B3LYP/cc-pVTZ have been rendered at different isovalues; The corresponding isovalues are indicated at the left column; The corresponding structure of each radical is also indicated at the top)

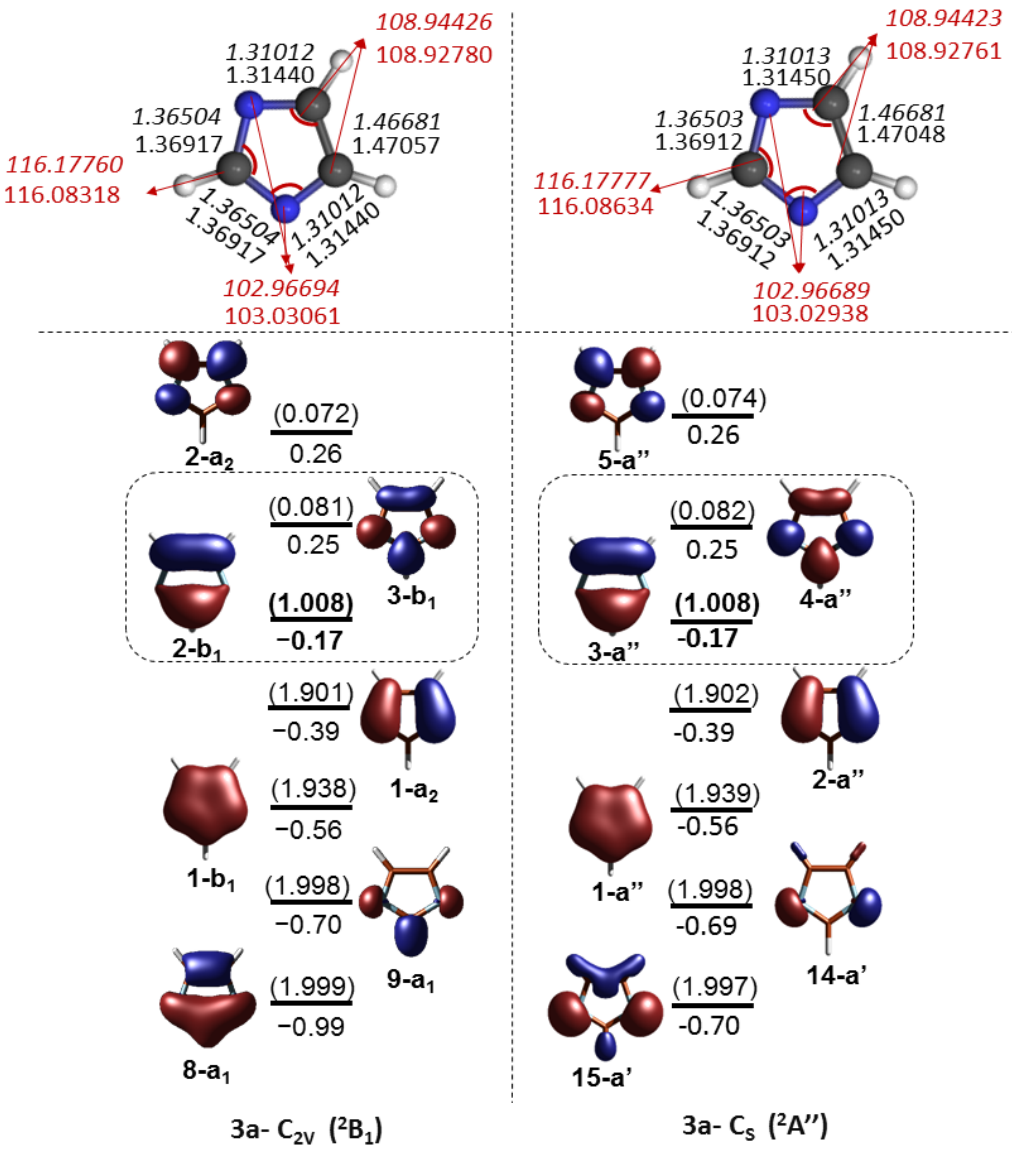
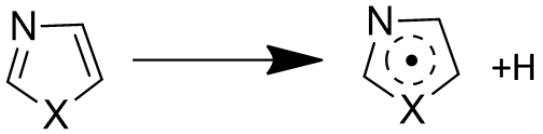


Figure 6S. The important geometrical parameters and molecular orbital diagram of **3a** corresponding to both C_{2v} and C_s symmetry. The normal font denotes bond lengths and bond angles obtained at (U)B3LYP/cc-pVTZ level of theory and the parameters in italics corresponds to the (U)M06-2X/cc-pVTZ level of theory. The MO orbitals are calculated at CASSCF/cc-pVTZ//(U)B3LYP/cc-pVTZ using Molpro. The active space orbitals are indicated along with their energies in hartrees and natural orbital occupancy numbers (NOON) in parentheses; the orbital symmetries are indicated below each one of them.

Table 4S: The energy difference between C_s and C_{2v} structure of **3a** at different levels of theory.

Level of theroy	Energy of C_s structure (Hartrees)	Energy of C_{2v} structure (Hartrees)	ΔE (C_s-C_{2v}) kcal/mol
UB3LYP/cc-pVTZ	–225.57940522	–225.57940420	–0.00062751
CCSD(T)/cc-pVTZ// UB3LYP/cc-pVTZ	–225.12538971	–225.12539012	0.00025720
(U)M06-2X/cc-pVTZ	–225.48605487	–225.48605487	0.00000000
CCSD(T)/cc-pVTZ// (U)M06-2X/cc-pVTZ	–225.12530511	–225.12530509	–0.00001255

TABLE 5S. The bond dissociation energy (BDE) values for the radical formation of all oxazole, thiazole and imidazole radical isomers, obtained from calculations at (U)B3LYP/cc-pVTZ level of theory.



Species		Enthalphy (Hartrees)	Enthalphy of parent (Hartrees)	BDE (kcal/mol)
Oxazole	**1b**	−245.41175	−246.09913	116.2
	1c	−245.41260		115.7
	1d	−245.40800		118.6
Thiazole	**2b**	−568.41163	−569.08615	108.1
	2c	−568.40711		111.0
	2d	−568.39903		116.1
Imidazole	**3a**	−225.57475	−226.22558	93.3
	3b	−225.54255		113.5
	3c	−225.54177		114.0
	3d	−225.53669		117.2

Enthalphy of Hydrogen atom at (U)B3LYP/cc-pVTZ = − 0.50216 Hartrees

Table 6S: Rate constant of all the reaction channels for both oxazole and thiazole radical as obtained from (U)B3LYP/cc-pVTZ level of theory. All rate constant values are in s^{-1}

S. No.	Species	Isomer	Reaction	$\Delta G_{product-reactant}$ (kcal/mol)	$\Delta S_{product-reactant}$ (cal/mol.K)	k (s^{-1})
1	**Oxazole**	1b	**1b-8**	18.90	6.96	5.77×10^{-14}
			8-10,11	-13.75	29.15	3.49×10^{6}
			1b-9	-13.46	7.36	8.64×10^{-7}
			9-10,11	18.61	28.75	2.59×10^{-6}
		1c	**1c-21**	-3.72	8.71	3.23×10^{-10}
			21-22	4.41	-1.59	1.15×10^{-22}
			22-25,26	-13.25	33.45	2.91×10^{3}
			1c-23	22.18	9.63	2.12×10^{-17}
			23-24	-14.58	-3.29	1.35×10^{-3}
			24-25,6	8.52	35.79	1.52×10^{-3}
		1d	**1d-36**	25.90	7.01	1.15×10^{-18}
			36-7,38	-36.18	34.14	3.06×10^{8}
			1d-37	-2.38	7.53	4.89
			37-7,38	-7.90	33.62	3.82×10^{3}
			1d-21	-6.58	8.62	3.84×10^{-19}
2	**thiazole**	2b	**2b-12**	19.78	8.37	4.58×10^{-13}
			12-11,14	-5.38	17.83	1.73×10^{10}
			2b-13	8.84	8.20	4.49×10^{-14}
			13-11,14	5.55	17.83	4.88×10^{-3}
			2b-15	6.56	6.25	1.33×10^{2}
			15-16	19.68	2.02	1.27×10^{-21}
			15-17	46.29	25.33	4.62×10^{-28}
			16-17	26.61	23.31	1.29×10^{-10}
		2c	**2c-27**	15.77	5.79	1.16×10^{-4}
			27-28	4.83	0.87	2.22×10^{-24}
			28-31,36	23.49	36.09	6.10×10^{-16}
			2c-29	32.57	8.75	1.70×10^{-21}
			29-30	-8.98	-1.4	5.94×10^{-6}
			30-7,32	-19.28	22.58	5.7×10^{9}
		2d	**2d-39**	18.67	8.51	6.34×10^{-14}
			39-7,32	-19.40	21.32	9.32×10^{10}
			2d-30	18.58	7.25	9.94×10^{-4}
			2d-27	8.65	7.29	2.08×10^{-29}
3	**imidazole**	3a	**3a-5**	48.43	6.66	1.7×10^{-30}
			5-6,7	12.06	35.61	9.86×10^{-8}
		3b	**3b-19**	16.58	7.69	1.45×10^{-21}
			19-20,11	-1.48	27.48	4.36
			3b-18	16.61	8.56	1.49×10^{-14}
			18-20,11	1.45	26.61	9.59×10^{-3}
		3c	**3c-33**	13.48	7.88	1.71×10^{-20}
			33-34	11.39	0.123	1.44×10^{-29}
			34-26,35	-0.87	35.79	1.28×10^{-4}
		3d	**3d-41**	21.33	7.87	8.16×10^{-17}
			41-26,7	-14.15	34.73	3.32×10^{3}
			3d-42	17.48	7.62	1.90×10^{-15}
			41-26,7	-10.30	34.98	3.35×10^{1}

Table 7S: Properties of reactants, intermediates, products and transition states of unimolecular decomposition pathways of dehydro-oxazole, thiazole and imidazole radicals at (U)B3LYP/cc-pVTZ levels of theory.

Species	Lowest harmonic frequency	Absolute energy (Hartrees)	ZVPE (Hartrees)	<S²> (annihilated)		Point Group	Electronic structure	ΔG (Hartrees)	ΔH (Hartrees)	Spin density
				Before	After					
3a	516.64	−225.6363	0.0567	0.7654	0.7502	C_S	^{2}B1	−225.6062	−225.5747	0.49 (C2); 0.35 (C4=C5)
TS_{3a-5}	380.29(i)	−225.5383	0.0519	0.7807	0.7505	C_1	^{2}A	−225.5137	−225.4811	0.92 (N1)
5	151.52	−225.5526	0.0521	0.7703	0.7502	C_1	^{2}A	−225.5290	−225.4944	0.97 (N1)
$TS_{5-6,7}$	447.73(i)	−225.5033	0.0473	0.7815	0.7505	C_1	^{2}A	−225.4860	−225.4491	0.49 (C2); 0.38 (C4)
6	427.53	−132.0498	0.0285	0.7711	0.7501	C_1	^{2}A	−132.0455	−132.0167	0.56 (C2); 0.56 (C4)
7	762.11	−93.46137	0.0163	0.0000	0.0000	$C_{\infty v}$	$^1\Sigma$	−93.4644	−93.4415	-
1b	563.70	−245.4616	0.0454	0.7577	0.7500	C_S	^{2}A′	−245.4429	−245.4117	0.87 (C2)
TS_{1b-8}	489.00(i)	−245.3998	0.0406	0.7866	0.7505	C_1	^{2}A	−245.3864	−245.3541	0.76 (C4); 0.39 (C2)
TS_{1b-9}	598.31(i)	−245.4153	0.0405	0.7721	0.7502	C_1	^{2}A	−245.4020	−245.3699	0.60 (C5); 0.49 (C2)
8	163.55	−245.4253	0.0409	0.7591	0.7500	C_S	^{2}A′	−245.4128	−245.3783	0.97 (C4)
9	123.32	−245.4775	0.0418	0.7610	0.7500	C_S	^{2}A′	−245.4644	−245.4297	0.99 (C5)
$TS_{8-10,11}$	568.62(i)	−245.4072	0.0377	0.7715	0.7503	C_1	^{2}A	−245.3993	−245.3630	0.59 (C4); 0.21 (N3) 0.34 (O1)
$TS_{9-10,11}$	303.92(i)	−245.4321	0.0381	0.7641	0.7501	C_1	^{2}A	−245.4245	−245.3874	0.38 (C5); 0.49 (N3) 0.19 (O1)
10	509.64	−168.0673	0.0100	0.7624	0.7501	$C_{\infty v}$	-	−168.0793	−168.0536	0.36 (O1); 0.71 (N3)
11	649.92	−77.3635	0.0269	0.0000	0.0000	$D_{\infty H}$	$^1\Sigma_g$	−77.3555	−77.3328	-
2b	446.13	−568.4589	0.0424	0.7566	0.7500	C_S	^{2}A′	−568.4443	−568.4116	0.73 (C2)
TS_{2b-12}	424.72(i)	−568.3990	0.0376	0.7749	0.7503	C_1	^{2}A	−568.3897	−568.3558	0.76 (C4); 0.32 (C2)
TS_{2b-13}	409.39(i)	−568.3980	0.0387	0.7913	0.7505	C_1	^{2}A	−568.3875	−568.3541	0.73 (C5); 0.37 (C2)
TS_{2b-15}	447.60(i)	−568.4324	0.0392	0.7665	0.7501	C_1	^{2}A	−568.4214	−568.3879	0.64 (S1); 0.21 (C2) 0.16 (C4)
12	131.29	−568.4202	0.0374	0.7604	0.7501	C_1	^{2}A	−568.4128	−568.3761	0.96 (C4)
13	66.47	−568.4393	0.0392	0.7627	0.7501	C_1	^{2}A	−568.4302	−568.3936	1.01 (C5)
15	112.18	−568.4451	0.0408	0.7543	0.7500	C_1	^{2}A	−568.4338	−568.3982	0.99 (S1)
15a	112.54	-568.4263	0.0404	0.7553	0.7500	C_1	^{2}A	-568.4159	-568.3795	0.57 (C5); 0.36 (S1)
15b	290.60	-132.1084	0.0306	0.7611	0.7501	C_1	^{2}A	-132.1022	-132.0731	0.82 (C4); 0.32 (C5)
$TS_{12-14,11}$	335.00(i)	−568.4117	0.0356	0.7714	0.7502	C_1	^{2}A	−568.4072	−568.3691	0.51 (C4); 0.56 (S1) 0.13 (N3)
$TS_{13-14,11}$	502.90(i)	−568.4023	0.0359	0.7735	0.7503	C_1	^{2}A	−568.3974	−568.3596	0.48 (C5); 0.38 (S1) 0.29 (N3)
TS_{15-16}	1742.73(i)	−568.3638	0.0335	0.7630	0.7501	C_1	^{2}A	−568.3607	−568.3235	0.68 (C5); 0.39 (S1)
16	110.75	−568.4099	0.0374	0.7573	0.7500	C_1	^{2}A	−568.4025	−568.3659	0.76 (C5); 0.19 (S1)
TS_{16-17}	114.12(i)	−568.3499	0.0293	0.7528	0.7500	C_1	^{2}A	−568.3531	−568.3129	0.97 (H)
TS_{15-17}	600.09(i)	−568.3461	0.0303	0.7631	0.7500	C_1	^{2}A	−568.3466	−568.3088	0.20 (S1); 0.91 (H)
TS_{15-15a}	1454.78(i)	-568.3737	0.0356	0.7543	0.7500	C_1	^{2}A	-568.3678	-568.3319	0.33 (C5); 0.54 (S1)
$TS_{15a-15b,31}$	180.54(i)	-568.3682	0.0354	0.7682	0.7502	C_1	^{2}A	-568.3647	-568.3255	0.70 (C4); 0.29 (C1); 0.08 (S1)
14	434.22	−491.0548	0.0072	0.7664	0.7501	$C_{\infty v}$	^{2}A	−491.0658	−491.0434	0.45 (C4); 0.67 (S1)
17	119.78	−567.8477	0.0291	0.0000	0.0000	C_S	^{1}A′	−567.8472	−567.8126	-
3b	445.16	−225.6054	0.0619	0.7563	0.7500	C_S	^{2}A′	−225.5742	−225.5425	0.82 (C2)
TS_{3b-19}	587.82(i)	−225.5257	0.0520	0.7815	0.7503	C_1	^{2}A	−225.3994	−225.367	0.71 (C5); 0.40 (C2)
19	134.55	−225.5653	0.0514	0.7614	0.7501	C_1	^{2}A	−225.5430	−225.5077	0.99 (C5)
$TS_{19-20,11}$	507(i)	−225.5355	0.0490	0.7752	0.7504	C_1	^{2}A	−225.5166	−225.4797	0.48 (C5); 0.30 (N1) 0.43 (N3)
20	471.21	−148.1868	0.0196	0.7720	0.7503	C_S	^{2}A″	−148.1909	−148.1629	0.62 (N1); 0.58 (N3)
TS_{3b-18}	467.38(i)	−225.5417	0.0531	0.7847	0.7505	C_1	^{2}A	−225.5163	−225.4832	0.38 (C2); 0.78 (C4)

18	153.46	−225.5718	0.0532	0.7598	0.7500	C_S	$^2A''$	−225.5478	−225.5121	0.98 (C4)
$TS_{18\text{-}20,11}$	537.37(i)	−225.5351	0.0495	0.7760	0.7504	C_1	^2A	−225.5155	−225.4791	0.49 (C4); 0.48 (N1) 0.27 (N3)
1c	601.48	−245.4628	0.0458	0.7569	0.7500	C_S	$^2A'$	−245.4437	−245.4126	0.89 (C4)
$TS_{1c\text{-}21}$	802.07(i)	−245.4081	0.0401	0.7661	0.7501	C_1	^2A	−245.3954	−245.3628	0.41 (C4); 0.24 (N3)
21	89.67	−245.4609	0.0403	0.7671	0.7671	C_1	^2A	−245.4497	−245.4144	0.59 (C5); 0.46 (N3)
$TS_{1c\text{-}23}$	347.83(i)	−245.3926	0.0401	0.7615	0.7615	C_1	^2A	−245.3797	−245.3474	0.79 (C4); 0.17 (C2)
23	61.77	−245.4181	0.0389	0.7699	0.7501	C_1	^2A	−245.4084	−245.3727	0.62 (C4); 0.48 (C2)
$TS_{21\text{-}22}$	1997.32(i)	−245.3739	0.0352	0.7571	0.7500	C_1	^2A	−245.3672	−245.3326	0.40 (C2); 0.24 (N3)
22	154.28	−245.4568	0.0426	0.7535	0.7500	C_1	^2A	−245.4426	−245.4081	0.66 (C2); 0.29 (O1)
$TS_{23\text{-}24}$	1059.71(i)	−245.3819	0.0357	0.7587	0.7500	C_1	^2A	−245.3744	−245.3402	0.68 (C2)
24	186.57	−245.4443	0.0408	0.7551	0.7500	C_1	^2A	−245.4316	−245.3975	0.64 (C5); 0.29 (O1)
$TS_{22\text{-}25,26}$	568.86(i)	−245.4319	0.0386	0.7678	0.7502	C_1	^2A	−245.4224	−245.3869	0.33 (C5); 0.28 (C2) 0.39 (N3)
$TS_{24\text{-}25,6}$	277.01(i)	−245.4043	0.0359	0.7746	0.7503	C_1	^2A	−245.3987	−245.3614	0.42 (C4); 0.48 (C2) 0.12 (C5)
25	2211.73	−113.3573	0.0050	0.0000	0.0000	$C_{\infty v}$	$^1\Sigma$	−113.3713	−113.3489	-
26	341.63	−132.0978	0.0294	0.7686	0.7501	C_1	^2A	−132.0924	−132.0635	0.64 (C5); 0.54 (N3)
2c	466.02	−568.4542	0.0423	0.7572	0.7500	C_S	$^2A'$	−568.4396	−568.4071	0.86 (C4)
$TS_{2c\text{-}27}$	311.47(i)	−568.4147	0.0396	0.7649	0.7501	C_1	^2A	−568.4033	−568.3699	0.51 (C4); 0.69 (C2)
27	143.75	−568.4267	0.0385	0.7919	0.7507	C_1	^2A	−568.4178	−568.3818	0.98 (S1)
$TS_{2c\text{-}29}$	269.12(i)	−568.3756	0.0374	0.7728	0.7503	C_1	^2A	−568.3668	−568.3327	0.74 (C4); 0.23 (C2)
29	78.44	−568.3950	0.0374	0.7977	0.7508	C_1	^2A	−568.3877	−568.3510	0.33 (C4); 0.61 (S1) 0.26 (C2)
$TS_{27\text{-}28}$	1974.79(i)	−568.3391	0.0335	0.7566	0.7500	C_1	^2A	−568.3354	−568.2993	0.34 (S1); 0.33 (C2) 0.19 (N3)
28	123.02	−568.4180	0.0407	0.7556	0.7500	C_1	^2A	−568.4068	−568.3711	0.41 (S1); 0.56 (C2)
$TS_{29\text{-}30}$	889.82(i)	−568.3506	0.0328	0.7601	0.7501	C_1	^2A	−568.3486	−568.3109	0.69 (C2)
30	103.00	−568.4112	0.0388	0.7561	0.7500	C_1	^2A	−568.4021	−568.3660	0.55 (C5); 0.37 (S1)
$TS_{28\text{-}26,31}$	359.29(i)	−568.3502	0.0352	0.7768	0.7505	C_1	^2A	−568.3459	−568.3081	0.47 (C5); 0.11 (S1) 0.11 (C2); 0.46 (N3)
$TS_{30\text{-}7,32}$	489.76(i)	−568.4009	0.0359	0.7593	0.7501	C_1	^2A	−568.3955	−568.3584	0.25 (C4); 0.11 (C5) 0.34 (S1); 0.27 (C2)
31	1304.18	−436.2593	0.0029	0.0000	0.0000	$C_{\infty v}$	$^1\Sigma$	−436.2769	−436.2530	-
32	367.75	−474.9660	0.0167	0.7653	0.7501	$C_{\infty v}$	-	−474.9684	−474.9445	0.67 (S1); 0.45 (C4)
3c	548.94	−225.6048	0.0584	0.7561	0.7500	C_S	$^2A'$	−225.5732	−225.5418	0.88 (C4)
$TS_{3c\text{-}33}$	634.03(i)	−225.5276	0.0526	0.7693	0.7502	C_1	^2A	−225.5024	−225.4698	0.35 (C4); 0.25 (N1) 0.27 (N3)
33	120.20	−225.5756	0.0527	0.7784	0.7505	C_S	$^2A''$	−225.5517	−225.5165	0.51 (C5); 0.30 (N1) 0.45 (N3)
$TS_{33\text{-}34}$	2152.50(i)	−225.4794	0.0470	0.7616	0.7501	C_1	^2A	−225.4612	−225.4261	0.44 (C2); 0.22 (N1) 0.29 (N3)
34	128.08	−225.5581	0.0531	0.7534	0.7500	C_S	$^2A'$	−225.5336	−225.4983	0.73 (C2); 0.20 (N1)
$TS_{34\text{-}26,35}$	513.79(i)	−225.5162	0.0488	0.7698	0.7503	C_1	^2A	−225.4973	−225.4606	0.23 (C2); 0.37 (C5) 0.44 (N3)
35	470.81	−93.4386	0.0156	-	-	$C_{\infty v}$	$^1\Sigma$	−93.4425	−93.4192	
1d	540.16	−245.4579	0.0455	0.7594	0.7500	C_S	$^2A'$	−245.4392	−245.4079	0.93 (C5)
$TS_{1d\text{-}36}$	466.90(i)	−245.3861	0.0409	0.8002	0.7506	C_1	^2A	−245.3725	−245.3402	0.42 (C5); 0.76 (N3)
36	160.52	−245.4103	0.0409	0.7577	0.7500	C_1	^2A	−245.3979	−245.3634	0.96 (N3)

TS_{1d-37}	383.14(i)	−245.4266	0.0409	0.7598	0.7500	C_1	^2A	−245.4129	−245.3806	0.68 (C5); 0.29 (C2)
37	148.47	−245.4553	0.0410	0.7548	0.7500	C_1	^2A	−245.4429	−245.4082	0.71 (C2); 0.18 (N3)
TS_{1d-21}	340.38(i)	−245.3808	0.0376	0.7674	0.7502	C_1	^2A	−245.3714	−245.3375	0.51 (C5); 0.45 (N3) 0.15 (O1)
$TS_{36-7,38}$	862.91(i)	−245.3966	0.0374	0.7722	0.7503	C_1	^2A	−245.3885	−245.3528	0.25 (C4); 0.64 (N3) 0.27 (O1)
$TS_{37-7,38}$	460.97(i)	−245.4306	0.0374	0.7595	0.7500	C_1	^2A	−245.4229	−245.3864	0.39 (C4); 0.29 (C2)
38	482.88	−151.9864	0.0188	0.7577	0.7500	C_S	$^2A'$	−151.9912	−151.9633	0.70 (C4); 0.29 (O1)
2d	418.32	−568.4463	0.0425	0.7592	0.7500	C_S	$^2A'$	−568.4316	−568.3990	0.93 (C5)
TS_{2d-39}	458.94(i)	−568.3849	0.0379	0.7820	0.7504	C_1	^2A	−568.3752	−568.3415	0.35 (C5); 0.75 (N3)
39	126.60	−568.4092	0.0372	0.7605	0.7501	C_1	^2A	−568.4019	−568.3652	0.14 (S1); 0.90 (N3)
TS_{2d-30}	156.97(i)	−568.4068	0.0379	0.7664	0.7501	C_1	^2A	−568.3973	−568.3632	0.55 (C5); 0.37 (C2)
TS_{2d-27}	390.04(i)	−568.3478	0.0353	0.7899	0.7506	C_1	^2A	−568.3416	−568.3066	0.33 (C5); 0.55 (S1) 0.36 (N3)
$TS_{39-7,32}$	455.96(i)	−568.4024	0.0352	0.7765	0.7504	C_1	^2A	−568.3979	−568.3602	0.19 (C4); 0.47 (S1) 0.57 (N3)
3d	456.98	−225.5996	0.0582	0.7511	0.7500	C_S	$^2A'$	−225.5683	−225.5367	0.91 (C5)
TS_{3d-40}	451.13 (i)	−225.5312	0.0534	0.7921	0.7506	C_S	$^2A'$	−225.5055	−225.4724	0.38 (C5); 0.80 (N3)
40	156.51	−225.5587	0.0533	0.7583	0.7500	C_S	$^2A'$	−225.5343	−225.4989	0.98 (N3)
$TS_{40-26,7}$	645.24(i)	−225.5344	0.0495	0.7774	0.7505	C_1	^2A	−225.5141	−225.4783	0.37 (C4); 0.42 (N1) 0.47 (N3)
TS_{3d-41}	373.81 (i)	−225.5327	0.0517	0.7694	0.7501	C_1	^2A	−225.5084	−225.4756	0.47 (C2); 0.49 (C5)
41	126.80	−225.5642	0.0527	0.7545	0.7500	C_1	^2A	−225.5404	−225.5052	0.69 (C2); 0.19 (N3)
$TS_{41-26,7}$	560.22 (i)	−225.5350	0.0488	0.7667	0.7502	C_1	^2A	−225.5159	−225.4794	0.36 (C2); 0.44 (C4) 0.24 (N1)

Table 8S. Properties of reactants, intermediates, products and transition states of unimolecular decomposition pathways of dehydro-oxazole, thiazole and imidazole radicals at (U)M06-2X/cc-pVTZ level of theory

Species	Lowest Harmonic frequency	Absolute energy (Hartrees)	ZVPE (Hartrees)	$<S^2>$ (annihilated)		Point Group	Electronic structure	ΔG (Hartrees)	ΔH (Hartrees)	Spin density
				Before	After					
3a	530.09	-225.5436	0.0575	0.7645	0.7501	C_{2V}	$^2B1$	-225.5122	-225.4815	0.51 (C2); 0.35 (C4=C5)
TS_{3a-5}	431.30(i)	-225.4325	0.0526	0.7853	0.7506	C_1	^2A	-225.4072	-225.3748	0.99 (N1)
5	147.74	-225.4466	0.0527	0.7834	0.7504	C_1	^2A	-225.4224	-225.3878	1.07 (N1)
$TS_{5-6,7}$	520.16(i)	-225.3956	0.0482	0.7954	0.7510	C_1	^2A	-225.3769	-225.3406	0.59 (C2); 0.32 (C4) 0.31 (N1)
6	402.52(i)	-131.9796	0.2775	0.7782	0.7501	C_1	^2A	-131.9757	-225.9474	0.58 (C2= C4)
7						$C_{\infty v}$	$^1\Sigma$			-
1b	619.20	-245.37124	0.0464	0.7607	0.7501	C_S	$^2A'$	-245.3515	-245.3204	0.95 (C2)
TS_{1b-8}	651.69(i)	-245.3003	0.0414	0.7930	0.7509	C_1	^2A	-245.2860	-245.2539	0.83 (C4); 0.43 (C2)
TS_{1b-9}	778.28(i)	-245.3115	0.0412	0.7832	0.7504	C_1	^2A	-245.2975	-245.2655	0.68 (C5); 0.51 (C2)
8	165.33	-245.3312	0.0419	0.7654	0.7501	C_S	$^2A'$	-245.3177	-245.2834	1.07(C4)
9	104.49	-245.3761	0.0425	0.7685	0.7501	C_S	$^2A'$	-245.3624	-245.3276	1.08 (C5)
$TS_{8-10,11}$	643.43(i)	-245.2993	0.0379	0.7765	0.7505	C_1	^2A	-245.2898	-245.2558	0.59 (C4); 0.24 (N3) (O1)
$TS_{9-10,11}$	402.12(i)	-245.3238	0.0387	0.7676	0.7502	C_1	^2A	-245.3152	-245.2786	0.43 (C5); 0.53 (N3) 0.19(O1)
10	542.59	-167.9994	0.0104	0.7664	0.7501	$C_{\infty v}$	-	-168.0109	-167.9853	0.34 (O1); 0.74 (N3)
11	711.31	-77.3245	0.0275	0.0000	0.0000	$D_{\infty H}$	$^1\Sigma_g$	-77.3159	-77.2933	-
2b	457.37	-568.3579	0.0430	0.7591	0.7500	C_S	$^2A'$	-568.3427	-568.3101	0.83 (C2)
TS_{2b-12}	553.33(i)	-568.2931	0.0384	0.7806	0.7506	C_1	^2A	-568.2830	-568.2494	0.83(C4); 0.35(C2)
TS_{2b-13}	508.13(i)	-568.2888	0.0393	0.8033	0.7510	C_1	^2A	-568.2776	-568.2443	0.82 (C5); 0.38 (C2)
TS_{2b-15}	357.27(i)	-568.3275	0.0406	0.7602	0.7501	C_1	^2A	-568.3152	-568.2817	0.81 (S1); 0.06 (C2) 0.13 (N3)
12	144.24	-568.3178	0.0385	0.7680	0.7501	C_1	^2A	-568.3089	-568.2728	1.08 (C4)
13	57.08	-568.3311	0.0397	0.7720	0.7501	C_1	^2A	-568.3215	-568.2849	1.09 (C5)
15	117.33	-568.3428	0.0415	0.7542	0.7500	C_1	^2A	-568.3307	-568.2953	0.99 (S1)
15a	110.71	-568.3226	0.0412	0.7567	0 . 7500	C_1	^2A	-568.3114	-568.2751	0.61(C5); 0.34(S1)
15b	303.60	-132.0482	0.0307	0.7624	0.7501	C_1	^2A	-132.0418	-132.0127	0.92 (C4); 0.31(C5)
$TS_{12-14,11}$	362.31(i)	-568.3036	0.0364	0.7724	0.7503	C_1	^2A	-568.2977	-568.2604	0.55 (C4); 0.59 (S1) 0.10 (N3)
$TS_{13-14,11}$	586.95(i)	-568.2869	0.0364	0.7812	0.7506	C_1	^2A	-568.2815	-568.2438	0.54 (C5);0.38 (S1) 0.31(N3)
TS_{15-16}	Channel not found					C_1	^2A			(C5); (S1)
16	106.69	-568.3051	0.0381	0.7620	0.7501	C_1	^2A	-568.2969	-568.2605	0.85(C5); 0.17 (S1)
TS_{16-17}	Channel not found					C_1	^2A			(H)
TS_{15-17}	842.20 (i)	-568.24049	0.0311	0.7662	0.7500	C_1	^2A	-568.2397	-568.2025	0.23 (S1); 0.89 (H)
TS_{15-15a}	1395.10(i)	-568.2686	0.0364	0.7543	0.7500	C_1	^2A	-568.2618	-568.2261	0.32(C5); 0.57(S1)
$TS_{15a-15b,31}$	294.77(i)	-568.2613	0.0359	0.7714	0.7503	C_1	^2A	-568.2569	-568.2182	0.78(C4); 0.12(S1); 0.27 (C1)
14	349.63	-490.9820	0.0081	0.7654	0.7501	$C_{\infty v}$	^2A	-490.9972	-490.9698	0.33 (N3); 0.83 (S1)
17	128.50	-567.74793	0.0297	0.0000	0.0000	C_S	$^1A'$	-567.7468	-567.7123	-
3b	495.90	-225.5159	0.05919	0.7593	0.7500	C_S	$^2A'$	-225.4835	-225.4521	0.93(C2)
TS_{3b-19}	740.70 (i)	-225.4248	0.0527	0.7892	0.7506	C_1	^2A	-225.3994	-225.3669	0.79 (C5); 0.42 (C2)
19	194.91	-225.4663	0.0521	0.7697	0.7501	C_1	^2A	-225.4434	-225.4079	1.08 (C5)
$TS_{19-20,11}$	578.93 (i)	-225.4294	0.0495	0.7787	0.7506	C_1	^2A	-225.4099	-225.3732	0.54 (C5); 0.31 (N1) 0.48 (N3)

20	475.61	-147.1199	0.0194	0.7770	0.7502	C_S	$^2A''$	-148.1242	-148.0962	0.68 (N1); 0.59(N3)
TS_{3b-18}	621.69 (i)	-225.4433	0.0539	0.7907	0.7508	C_1	^2A	-225.4169	-225.3841	0.41 (C2); 0.85 (C4)
18	90.37	-225.4782	0.0538	0.7664	0.7501	C_S	$^2A''$	-225.4528	-225.4185	1.08 (C4)
$TS_{18-20,11}$	584.66 (i)	-225.4314	0.0501	0.7770	0.7505	C_1	^2A	-225.4112	-225.3747	0.54 (C4); 0.56(N1) 0.26 (N3)
1c	620.83	-245.37171	0.0467	0.7604	0.7500	C_S	$^2A'$	-245.3517	-245.3206	0.9958 (C4)
TS_{1c-21}	319.12(i)	-245.3009	0.0414	0.7656	0.7501	C_1	^2A	-245.2868	-245.2545	0.42 (C4); 0.49(O1) 0.07 (C5)
21	94.70	-245.3566	0.0412	0.7735	0.7503	C_1	^2A	-245.3443	-245.3092	0.71 (C5); 0.45 (N3)
TS_{1c-23}	396.96(i)	-245.2835	0.0401	0.7627	0.7501	C_1	^2A	-245.2711	-245.2379	0.90 (C4); 0.12(C2)
23	67.76	-245.3062	0.0397	0.7778	0.7504	C_1	^2A	-245.2955	-245.2601	0.79 (C4); 0.36 (C2)
TS_{21-22}	1884.24(i)	-245.2714	0.0364	0.7587	0.7500	C_1	^2A	-245.2635	-245.2291	0.41(C2); 0.24(N3) 0.19 (O1)
22	158.32	-245.3573	0.043261	0.7541	0.7500	C_1	^2A	-245.3425	-245.3080	0.68 (C2); 0.27 (O1)
TS_{23-24}	1041.73(i)	-245.2719	0.0366	0.7632	0.7501	C_1	^2A	-245.2636	-245.2295	0.73 (C2)
24	188.51	-245.3353	0.0412	0.7581	0.7500	C_1	^2A	-245.3222	-245.2880	0.67 (C5); 0.28 (O1)
$TS_{22-25,26}$	611.74(i)	-245.3282	0.0392	0.7695	0.7503	C_1	^2A	-245.3180	-245.2827	0.37 (C5); 0.27(C2) 0.47 (N3)
$TS_{24-25,6}$	337.87	-245.2945	0.0355	0.7807	0.7507	C_1	^2A	-245.2894	-245.2518	0.68 (C4); 0.29 (C2) 0.11 (C5)
25	2263.37	-113.3188	0.0052	0.0000	0.0000	$C_{\infty v}$	$^1\Sigma$	-113.3328	-113.3104	-
26	421.43	132.0326	0.0298	0.7744	0.7502	C_1	^2A	-132.0268	-131.9980	0.76 (C5); 0.55 (N3)
2c	479.06	-568.3543	0.0429	0.7609	0.7501	C_S	$^2A'$	-568.3389	-568.3065	0.95(C4)
TS_{2c-27}	348.73(i)	-568.3067	0.0403	0.7661	0.7501	C_1	^2A	-568.2945	-568.2614	0.36 (C4);0.72 (S1)
27	110.47	-568.3177	0.0406	0.7546	0.7500	C_1	^2A	-568.3065	-568.2711	0.99 (S1)
TS_{2c-29}	318.10(i)	-568.2604	0.0373	0.7730	0.7503	C_1	^2A	-568.2523	-568.2173	0.82 (C4); 0.21 (C2)
29	66.97	-568.2648	0.0390	0.7545	0.7500	C_1	^2A	-568.2557	-568.2194	0.99 (S1)
TS_{27-28}	1861.22(i)	-568.2302	0.0344	0.7582	0.7500	C_1	^2A	-568.2254	-568.1896	0.35 (S1); 0.34 (C2) 0.17 (N3)
28	121.51	-568.3118	0.0413	0.7560	0.7500	C_1	^2A	-568.2999	-568.2644	0.41 (S1); 0.58 (C2)
TS_{29-30}	715.01 (i)	-568.23747	0.0338	0.7672	0.7502	C_1	^2A	-568.2334	-568.1969	0.77 (C2)
30	77.79	-568.2971	0.0386	0.7567	0.7500	C_1	^2A	-568.2888	-568.2519	0.56 (C5); 0.38 (S1)
$TS_{28-26,31}$	449.51(i)	-568.2355	0.0354	0.7807	0.7506	C_1	^2A	-568.2310	-568.1932	0.54(C5); 0.12 (S1) 0.53 (N3) (C2); (N3)
$TS_{30-7,32}$	443.19(i)	-568.2884	0.0366	0.7607	0.7501	C_1	^2A	-568.2819	-568.2453	0.19(C4); 0.15(C5) 0.34 (S1); 0.29(C2)
31	1332.74	-436.2102	0.0030	0.0000	0.0000	$C_{\infty v}$	$^1\Sigma$	-436.2277	-436.2039	-
32	389.98	-474.8932	0.0171	0.7700	0.7501	$C_{\infty v}$	-	-474.8948	-474.8714	0.69 (S1); 0.52 (C4)
3c	566.21	-225.5157	0.0594	0.7593	0.7500	C_S	$^2A'$	-225.4830	-225.4517	0.98 (C4)
TS_{3c-33}	821.89 (i)	-225.4240	0.0574	0.7623	0.7501	C_1	^2A	-225.3981	-225.3656	0.32 (C4); 0.27 (N1) 0.26 (N3)
33	100.55	-225.4735	0.0535	0.7815	0.7506	C_S	$^2A''$	-225.4489	-225.4137	0.64(C5); 0.27 (N1) 0.48 (N3)
TS_{33-34}	2067.16 (i)	-225.3802	0.0481	0.7621	0.7501	C_1	^2A	-225.3608	-225.3258	0.46 (C2); 0.23 (C5) 0.31 (N3)
34	123.89	-225.4608	0.0540	0.7543	0.7500	C_S	$^2A'$	-225.4354	-225.4003	0.78 (C2); 0.16 (N1)
$TS_{34-26,35}$	563.52 (i)	-225.4137	0.0494	0.7699	0.7503	C_1	^2A	-225.3938	-225.3574	0.22 (C2); 0.39 (C5) 0.50 (N3)
35	419.07	-132.0326	0.0298	0.7744	0.7502	$C_{\infty v}$	$^1\Sigma$	-132.0267	-131.9979	0.76 (C4); 0.55 (N1)

1d	588.46	-245.3676	0.0466	0.7628	0.7501	C_S	$^2A'$	-245.3477	-245.3166	1.0229 (C5)
TS_{1d-36}	660.69(i)	-245.2839	0.0416	0.8039	0.7511	C_1	^2A	-245.2695	-245.2374	0.48(C5);0.80 (N3)
36	170.56	-245.3138	0.0419	0.7608	0.7501	C_1	^2A	-245.3001	-245.2659	1.01 (N3)
TS_{1d-37}	400.08(i)	-245.3207	0.0414	0.7627	0.7501	C_1	^2A	-245.3065	-245.2744	0.71(C5); 0.30(C2)
37	147.67	-245.3509	0.0417	0.7566	0.7500	C_1	^2A	-245.3378	-245.3032	0.76(C2);0.14 (N3)
TS_{1d-21}	419.31(i)	-245.2781	0.0386	0.7710	0.7502	C_1	^2A	-245.2675	-245.2339	0.56 (C5); 0.46 (N3) 0.13 (O1)
$TS_{36-7,38}$	1139.33(i)	-245.2895	0.03801	0.7803	0.7506	C_1	^2A	-245.2804	-245.2452	0.29 (C4);0.63 (N3) 0.33 (O1)
$TS_{37-7,38}$	490.42(i)	-245.3236	0.0382	0.7623	0.7501	C_1	^2A	-245.3148	-245.2789	0.38(C4); 0.34(C2)
38	404.04	-151.9191	0.0190	0.7617	0.7501	C_S	$^2A'$	-151.9235	-151.8956	0.74(C4); 0.29 (O1)
2d	442.32	-568.3466	0.0433	0.7636	0.7501	C_S	$^2A'$	-568.3309	-568.2985	1.02 (C5)
TS_{2d-39}	567.17(i)	-568.2761	0.0386	0.7845	0.7507	C_1	^2A	-568.2657	-568.2321	0.39 (C5);0.80 (N3)
39	130.54	-568.3028	0.0381	0.7646	0.7501	C_1	^2A	-568.2945	-568.2581	0.13 (S1);0.97 (N3)
TS_{2d-30}	189.24(i)	-568.2939	0.0385	0.7648	0.7501	C_1	^2A	-568.2839	-568.2499	0.58 (C5); 0.32 (C2)
TS_{2d-27}	447.81(i)	-568.2382	0.0357	0.7954	0.7507	C_1	^2A	-568.2315	-568.1968	0.34 (C5); 0.57 (S1) 0.40 (N3)
$TS_{39-7,32}$	550.88(i)	-568.2928	0.0358	0.7795	0.7505	C_1	^2A	-568.2877	-568.2501	0.19 (C4); 0.49(S1) 0.59 (N3)
3d	502.01	-225.5101	0.0593	0.7612	0.7501	C_S	$^2A'$	-225.4776	-225.4462	1.02 (C5)
TS_{3d-40}	599.45 (i)	-225.4300	0.0539	0.7961	0.7509	C_S	$^2A'$	-225.4036	-225.3706	0.43 (C5); 0.85 (N3)
40	157.51	-225.4621	0.0540	0.7618	0.7501	C_S	$^2A'$	-225.4370	-225.4016	1.03 (N3)
$TS_{40-26,7}$	745.96 (i)	-225.4305	0.0503	0.7819	0.7507	C_1	^2A	-225.4093	-225.3738	0.41 (C4); 0.48 (N1) 0.50 (N3)
TS_{3d-41}	475.55 (i)	-225.4281	0.0523	0.7732	0.7502	C_1	^2A	-225.4032	-225.3705	0.55 (C2); 0.50 (C5)
41	132.76	-225.4624	0.0534	0.7561	0.7500	C_1	^2A	-225.4378	-225.4027	0.75 (C2); 0.15(N3)
$TS_{41-26,7}$	625.76 (i)	-225.4305	0.0495	0.7693	0.7502	C_1	^2A	-225.4104	-225.3743	0.41 (C2); 0.47 (C4) 0.24 (N1)