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

Through bond and through space interactions in dehydro-diazine radicals: A case study of 3c-5e interactions

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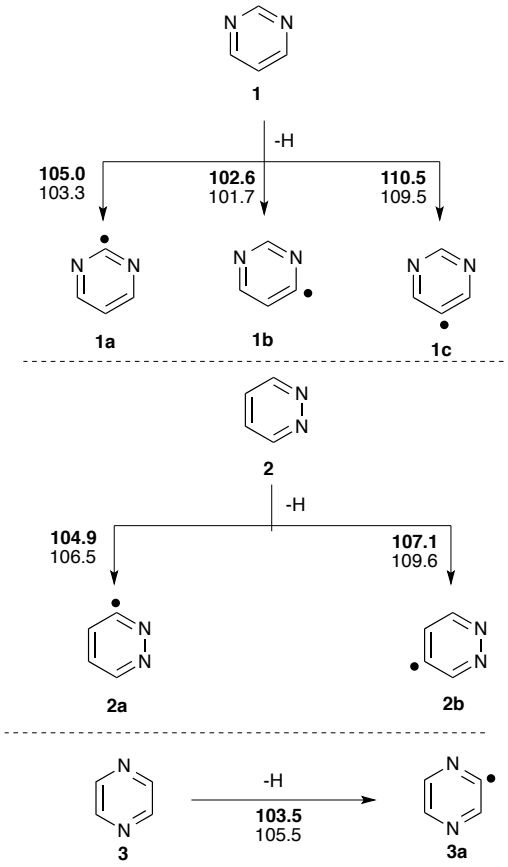
Table 1S. Electronic and thermodynamic parameters of the dehydrodiazine radical isomers and their respective parents at both (U)B3LYP/cc-pVTZ and (U)M06-2X/cc-pVTZ levels of theory.

Species	Absolute energy (Hartree)	ZPVE (Hartree)	Lowest frequency	Spin contamination		Point group	Electronic state	Free Energy (G) (Hartree)	Enthalpy (H) (Hartree)
				Before annhilation	After annhilation				
1	**−264.41609**	**0.076862**	**353.78**	**0.0000**	**0.0000**	C_{2v}	$^1A_1$	**−264.36592**	**−264.33411**
	−264.30610	*0.077782*	*359.03*	*0.0000*	*0.0000*			*−264.25500*	*−264.22322*
1a	**−263.73356**	**0.063775**	**382.06**	**0.7551**	**0.7500**	C_{2v}	$^2A_1$	**−263.69705**	**−263.66468**
	−263.62618	*0.064661*	*388.26*	*0.7589*	*0.7500*			*−263.58876*	*−263.55645*
1b	**−263.73754**	**0.063924**	**350.07**	**0.7548**	**0.7500**	C_s	$^2A'$	**−263.70152**	**−263.66852**
	−263.62889	*0.064711*	*352.46*	*0.7581*	*0.7500*			*−263.59207*	*−263.55911*
1c	**−263.72486**	**0.063895**	**381.53**	**0.7569**	**0.7500**	C_{2v}	$^2A_1$	**−263.68823**	**−263.65587**
	−263.61631	*0.064829*	*382.25*	*0.7622*	*0.7501*			*−263.57872*	*−263.54643*
2	**−264.38036**	**0.076045**	**377.37**	**0.0000**	**0.0000**	C_{2v}	$^1A_1$	**−264.33104**	**−264.29915**
	−264.26816	*0.076970*	*382.01*	*0.0000*	*0.0000*			*−264.21789*	*−264.18605*
2a	**−263.69779**	**0.062816**	**355.23**	**0.7551**	**0.7500**	C_s	$^2A'$	**−263.66294**	**−263.62977**
	−263.58708	*0.063763*	*360.92*	*0.7589*	*0.7500*			*−263.55125*	*−263.51818*
2b	**−263.69427**	**0.062837**	**375.83**	**0.7567**	**0.7500**	C_s	$^2A'$	**−263.65936**	**−263.62631**
	−263.58219	*0.063814*	*376.96*	*0.7623*	*0.7501*			*−263.54629*	*−263.51329*
3	**−264.40947**	**0.076650**	**351.84**	**0.0000**	**0.0000**	D_{2h}	^1A_g	**−264.35884**	**−264.32771**
	−264.29867	*0.077494*	*359.20*	*0.0000*	*0.0000*			*−264.24719*	*−264.21609*
3a	**−263.72956**	**0.063807**	**365.59**	**0.7553**	**0.7500**	C_s	$^2A'$	**−263.69366**	**−263.66067**
	−263.61943	*0.064602*	*372.68*	*0.7583*	*0.7500*			*−263.58271*	*−263.54977*

Normal font indicates (U)B3LYP/cc-pVTZ and italics represent (U)M06-2X/cc-pVTZ

Fig. 1S. Bond Dissociation Energies (BDEs) of the dehydrodiazine radical isomers at (U)B3LYP/cc-pVTZ and (U)M06-2x/cc-pVTZ levels of theory.

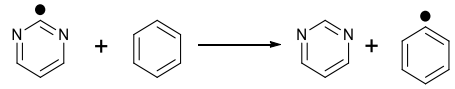
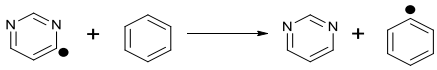
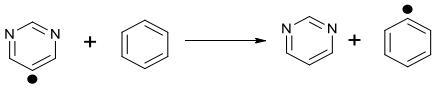
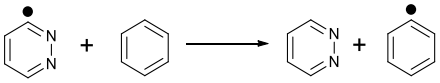
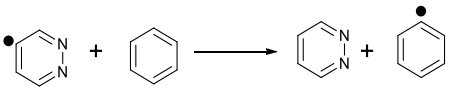
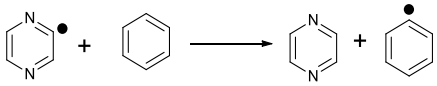


Bold- (U)B3LYP/cc-pVTZ and Normal font- (U)M06-2X/cc-pVTZ

Table 2S. Relative energies of isomeric dehydro-diazine radicals at (U)B3LYP level with different basis sets.

Level of theory	Relative energy (kcal/mol)					
	Dehydropyrimidine radicals			Dehydropyridazine radicals		Dehydropyrazine radicals
	1a	**1b**	**1c**	**2a**	**2b**	**3a**
(U)B3LYP/6-311++G(d,p)	2.5	0.0	7.8	24.7	26.8	4.9
(U)B3LYP/cc-pVDZ	2.2	0.0	7.8	23.9	25.8	4.8
(U)B3LYP/aug-cc-pVDZ	2.5	0.0	7.6	23.9	25.8	4.7
(U)B3LYP/cc-pVTZ	2.4	0.0	7.9	24.2	26.5	4.9
(U)B3LYP/aug-cc-pVTZ	2.5	0.0	7.9	24.3	26.5	4.9
(U)B3LYP/cc-pVQZ	2.4	0.0	8.0	24.3	26.6	4.9
(U)B3LYP/aug-cc-pVQZ	2.5	0.0	8.0	24.3	26.5	4.9

Table 3S. Radical stabilization energies (RSE) of the dehydrodiazine radical isomers based on isodesmic reaction

Reactant and products in the isodesmic reactions	ΔH_{298}
1a 	4.2 *3.8*
1b 	6.6 *5.5*
1c 	–1.3 *–2.5*
2a 	4.2 *3.1*
2b 	2.0 *0.04*
3a 	5.7 *4.1*

Normal font indicates (U)B3LYP/cc-pVTZ and italics represent (U)M06-2X/cc-pVTZ.

Figure 2S. Electrostatic potential mapping of the dehydrodiazine radical isomers along with their parent molecule at (U)B3LYP/cc-pVTZ level of theory.

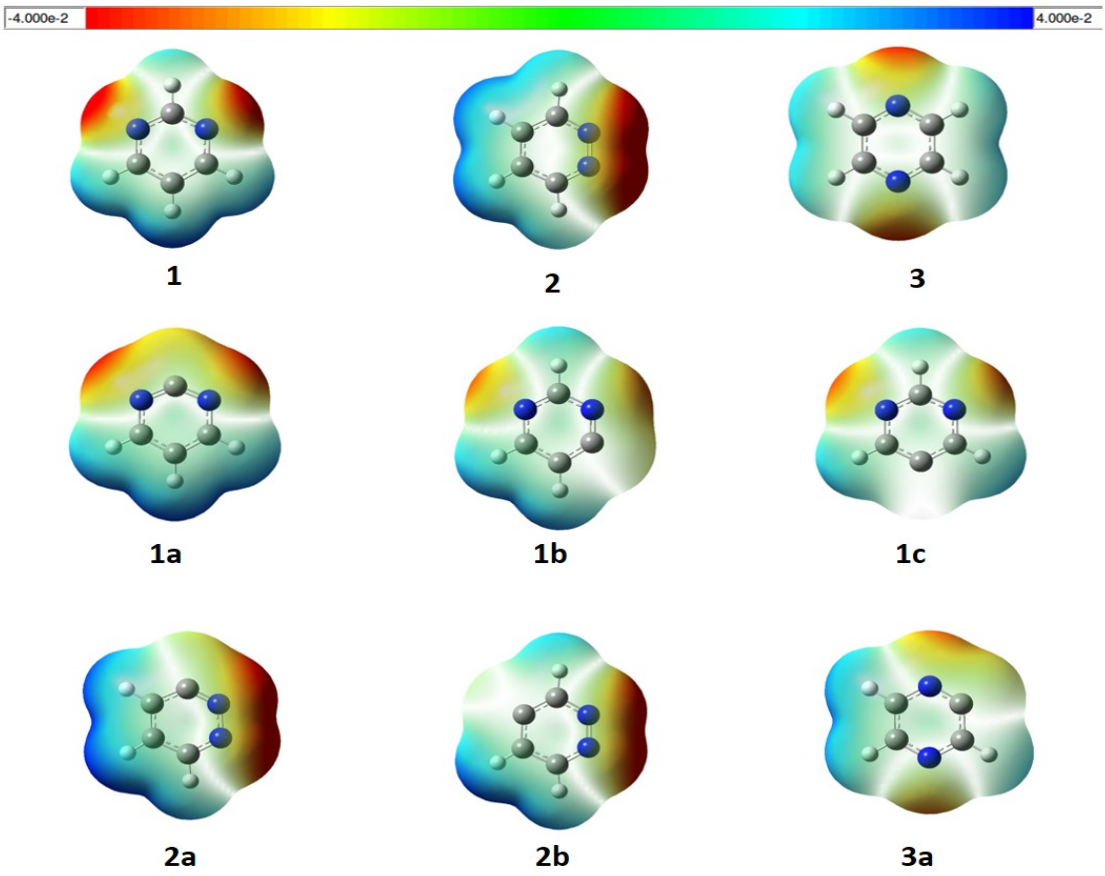


Table 4S. The second order perturbation energies (in kcal/mol) from the natural bond orbital (NBO) analysis of dehydrodiazine radical isomers. (Bold - (U)B3LYP/cc-pVTZ and italics-(U)M06-2X/cc-pVTZ and normal – (U)MP2/cc-pVTZ)

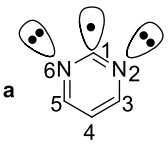
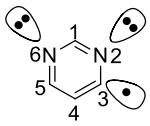
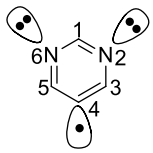
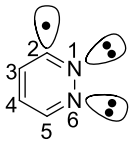
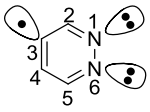
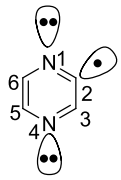
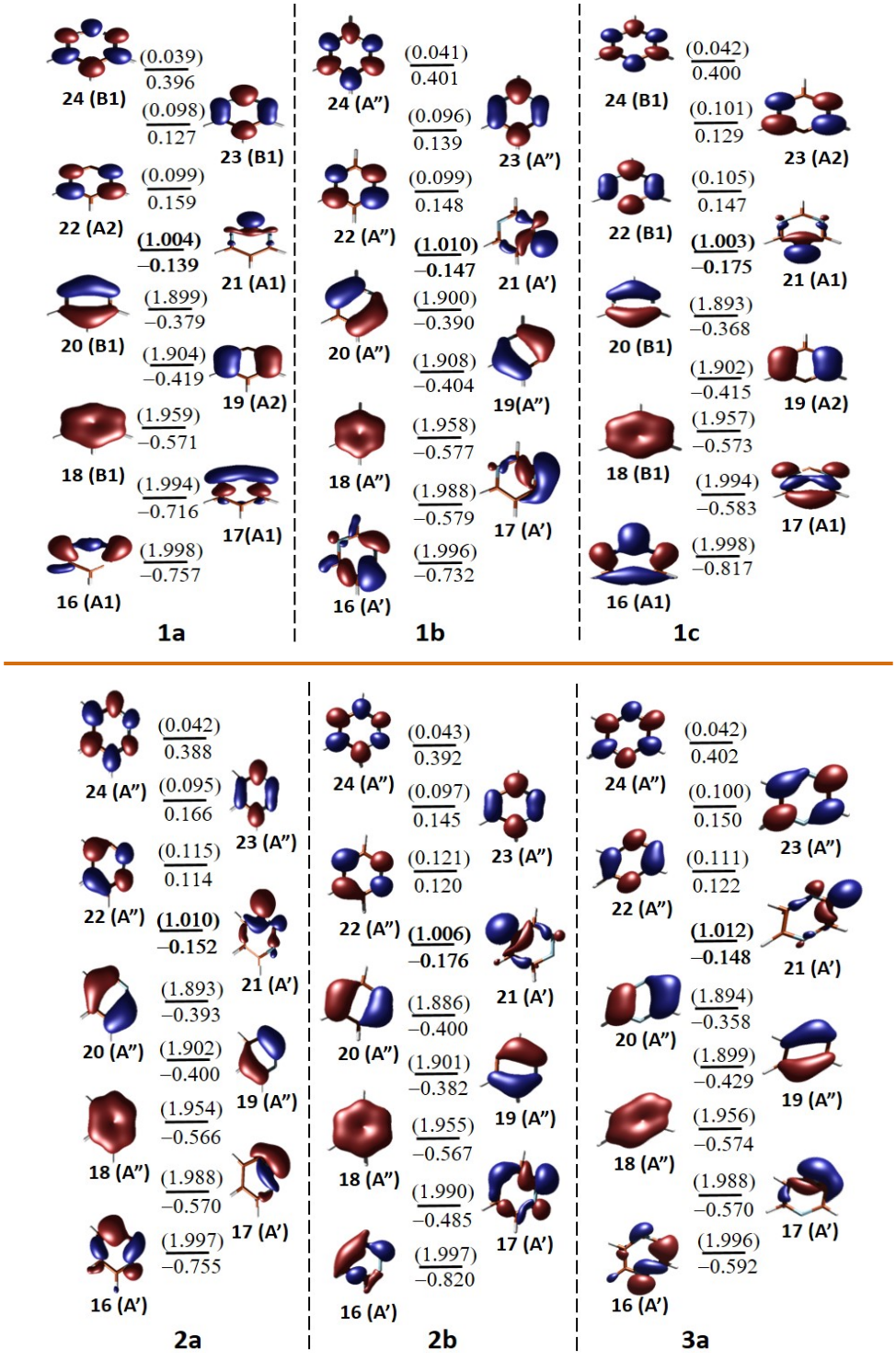
1a 			**1b** 			**1c** 		
Donor	Acceptor	$<E^2>$	Donor	Acceptor	$<E^2>$	Donor	Acceptor	$<E^2>$
		10.1			**17.2**			**0.8**
$n_{(N2)}$	$n^*_{(C1)}$	*12.5*	$n_{(N2)}$	$n^*_{(C3)}$	*23.2*	$n_{(N2)}$	$n^*_{(C4)}$	*1.1*
		13.8			25.9			1.0
		0.7			**5.6**			**5.6**
$n_{(N2)}$	$\pi^*_{(C1-N2)}$	*0.4*	$n_{(N2)}$	$\pi^*_{(C1-N6)}$	*6.5*	$n_{(N2)}$	$\pi^*_{(C1-N6)}$	*6.7*
					7.8			8.1
		4.1			**3.1**			**5.5**
$n_{(N2)}$	$\pi^*_{(C1-N6)}$	*4.9*	$n_{(N2)}$	$\pi^*_{(C3-C4)}$	*3.8*	$n_{(N2)}$	$\pi^*_{(C3-C4)}$	*6.2*
		6.3			5.5			6.8
		10.1						**0.8**
$n_{(N6)}$	$n^*_{(C1)}$	*12.5*	$n_{(N2)}$	$\pi^*_{(N2-C3)}$	**0.4**	$n_{(N6)}$	$n^*_{(C4)}$	*1.1*
		13.8						1.0
		4.1						**5.6**
$n_{(N6)}$	$\pi^*_{(C1-N2)}$	*4.9*	$n_{(N6)}$	$n^*_{(C3)}$	------	$n_{(N6)}$	$\pi^*_{(C1-N2)}$	*6.7*
		6.3						8.1
		0.7			**5.6**			**5.5**
$n_{(N6)}$	$\pi^*_{(C1-N6)}$	*0.4*	$n_{(N6)}$	$\pi^*_{(C4-C5)}$	*6.5*	$n_{(N6)}$	$\pi^*_{(C4-C5)}$	*6.2*
					7.2			6.8
		30.4			**23.3**			**26.5**
$\pi^*_{(C3-C4)}$	$\pi^*_{(C1-N2)}$	*33.6*	$\pi^*_{(C1-N6)}$	$\pi^*_{(N2-C3)}$	*29.6*	$\pi^*_{(C1-N2)}$	$\pi^*_{(C3-C4)}$	---
		19.0			24.5			41.0
		32.6			**36.4**			**33.6**
$\pi^*_{(C5-N6)}$	$\pi^*_{(C1-N2)}$	*38.6*	$\pi^*_{(C4-C5)}$	$\pi^*_{(N2-C3)}$	*38.2*	$\pi^*_{(C5-N6)}$	$\pi^*_{(C3-C4)}$	---
		23.7			24.4			43.7
2a 			**2b** 			**3a** 		
		23.7			**0.7**			**20.0**
$n_{(N1)}$	$n^*_{(C2)}$	*27.0*	$n_{(N1)}$	$n^*_{(C3)}$	*1.0*	$n_{(N1)}$	$n^*_{(C2)}$	*25.7*
		36.8			0.8			34.0
		3.8			**4.9**			
$n_{(N1)}$	$\pi^*_{(C2-C3)}$	*4.5*	$n_{(N1)}$	$\pi^*_{(C5-N6)}$	*5.9*	$n_{(N1)}$	$\pi^*_{(C2-N1)}$	**0.3**
		6.4			6.1			
		3.9			**5.9**			**3.1**
$n_{(N1)}$	$\pi^*_{(C5-N6)}$	*4.8*	$n_{(N1)}$	$\pi^*_{(C2-C3)}$	*6.6*	$n_{(N1)}$	$\pi^*_{(C2-C3)}$	*3.7*
		4.4			7.8			5.6
		0.6			**1.5**			**0.5**
$n_{(N6)}$	$n^*_{(C2)}$	*0.7*	$n_{(N6)}$	$\pi^*_{(N1-C2)}$	*7.2*	$n_{(N4)}$	$n^*_{(C2)}$	*0.8*
		0.6			7.0			0.9
		4.4						**5.0**
$n_{(N6)}$	$\pi^*_{(C2-N1)}$	*5.0*	$n_{(N6)}$	$n^*_{(C2)}$	------	$n_{(N4)}$	$\pi^*_{(C5-C6)}$	*5.8*
		4.8						6.0
					5.9			**6.4**
$n_{(N6)}$	$\pi^*_{(C5-N6)}$	**0.7**	$n_{(N6)}$	$\pi^*_{(C4-C5)}$	*6.9*	$n_{(N4)}$	$\pi^*_{(C2-C3)}$	*7.2*
					8.8			9.0
		29.2			**27.0**			**28.6**
$\pi^*_{(C3-C4)}$	$\pi^*_{(C2-N1)}$	*30.8*	$\pi^*_{(N1-C2)}$	$\pi^*_{(C3-C4)}$	*35.6*	$\pi^*_{(C5-C6)}$	$\pi^*_{(C2-N1)}$	*33.3*
		14.0			26.7			15.5
		15.6			**22.9**			**34.6**
$\pi^*_{(C5-N6)}$	$\pi^*_{(C2-N1)}$	*21.7*	$\pi^*_{(C5-N6)}$	$\pi^*_{(C3-C4)}$	*30.5*	$\pi^*_{(C3-N4)}$	$\pi^*_{(C2-N1)}$	*40.8*
		12.7			22.6			20.4

Fig. 3S. Molecular orbitals of all the dehydrodiazine radical isomers using multiconfigurational CASSCF method at /cc-pVTZ level of theory.



The complete active space molecular orbital diagrams of all the radicals at CASSCF/cc-pVTZ level of theory; The values in normal font indicate orbital energies (hartree) and values in parenthesis represent the occupancies. Orbital number and their respective symmetry are designated in bold. All the orbitals are rendered at an isovalue 0.05.

Table 5S. Isotropic hyperfine coupling constants of the two ^{14}N atoms and ^{13}C radical centres for all the six isomeric dehydrodiazine radical isomers at (U)B3LYP/EPR-III level of theory

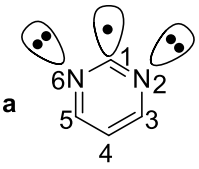
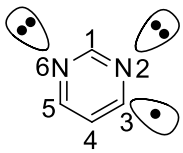
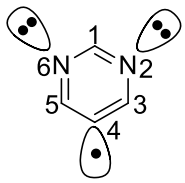
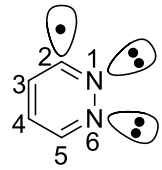
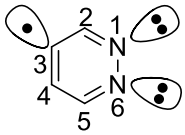
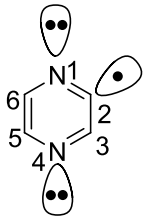
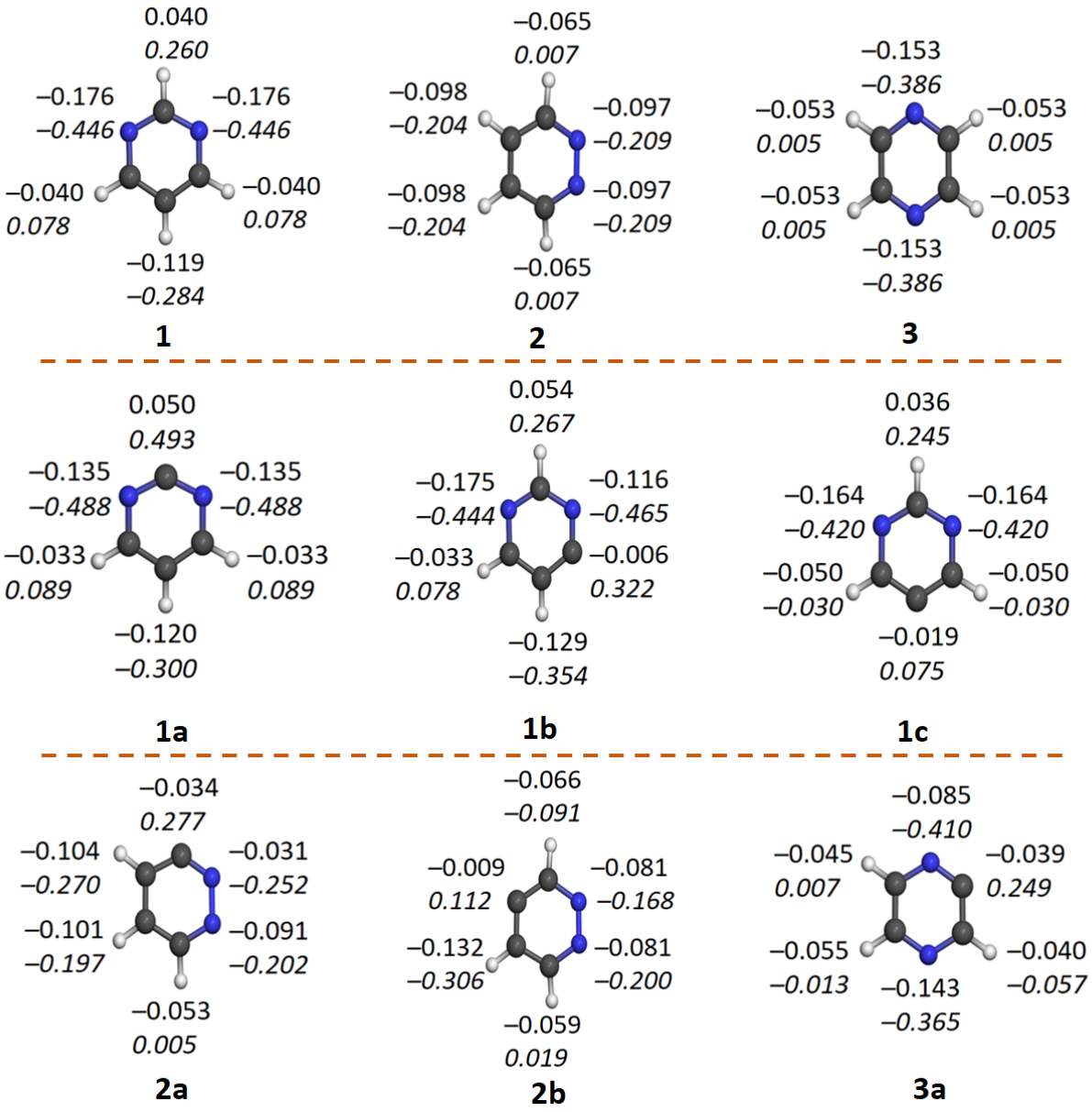
Species	Atoms	Isotropic Fermi interactions (Gauss)
1a 	1 (13C)	238.1357
	2 (14N)	35.2961
	6 (14N)	35.2961
1b 	3 (13C)	179.7258
	2 (14N)	32.7038
	6 (14N)	0.2303
1c 	4 (13C)	129.8207
	2 (14N)	-0.3898
	6 (14N)	-0.3898
2a 	2 (13C)	193.9606
	1 (14N)	42.6606
	6 (14N)	7.9425
2b 	3 (13C)	119.9123
	1 (14N)	0.3949
	6 (14N)	9.0094
3a 	2 (13C)	174.9364
	1 (14N)	33.9281
	4 (14N)	-0.3945

Fig. 4S. Natural and Mulliken charges of all the dehydrodiazine radical isomers and their respective parent using (U)B3LYP/cc-pVTZ level of theory. (Normal – Mulliken charges; Italics – Natural charges)



Appendix 1S. Cartesian coordinates of the optimized structures at different levels of theory.

Pyrimidine **1**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
C	0.00000000	0.00000000	-1.30664600	C	0.00000000	0.00000000	-1.29999100
N	0.00000000	1.19230000	-0.71243700	N	0.00000000	1.18737000	-0.70976500
C	0.00000000	1.18037100	0.62067600	C	0.00000000	1.17451600	0.61673200
C	0.00000000	0.00000000	1.34942300	C	0.00000000	0.00000000	1.34455100
C	0.00000000	-1.18037100	0.62067600	C	0.00000000	-1.17451600	0.61673200
N	0.00000000	-1.19230000	-0.71243700	N	0.00000000	-1.18737000	-0.70976500
H	0.00000000	2.14558700	1.11499400	H	0.00000000	2.13980100	1.11483300
H	0.00000000	0.00000000	-2.39068400	H	0.00000000	0.00000000	-2.38640300
H	0.00000000	0.00000000	2.43005300	H	0.00000000	0.00000000	2.42530100
H	0.00000000	-2.14558700	1.11499400	H	0.00000000	-2.13980100	1.11483300

2-Dehydropyrimidine **1a**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
C	0.00000000	0.00000000	1.32154000	C	0.00000000	0.00000000	1.31503800
N	0.00000000	1.18561100	0.78196500	N	0.00000000	1.18344600	0.77901800
C	0.00000000	1.18675000	-0.56039000	C	0.00000000	1.18069800	-0.55638200
C	0.00000000	0.00000000	-1.28130800	C	0.00000000	0.00000000	-1.27639700
C	0.00000000	-1.18675000	-0.56039000	C	0.00000000	-1.18069800	-0.55638200
N	0.00000000	-1.18561100	0.78196500	N	0.00000000	-1.18344600	0.77901800
H	0.00000000	2.15268800	-1.05132800	H	0.00000000	2.14619000	-1.05233200
H	0.00000000	0.00000000	-2.36157500	H	0.00000000	0.00000000	-2.35685000
H	0.00000000	-2.15268800	-1.05132800	H	0.00000000	-2.14619000	-1.05233200

4-Dehydropyrimidine **1b**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
C	-1.09887400	-0.69331400	0.00000000	C	-1.09130700	-0.69013700	0.00000000
N	0.05065900	-1.39545100	0.00000000	N	0.04878700	-1.39591400	0.00000000
C	1.14714800	-0.73325900	0.00000000	C	1.13874100	-0.72654500	0.00000000
C	1.23523400	0.64912800	0.00000000	C	1.23102600	0.64849500	0.00000000
C	0.00000000	1.28836900	0.00000000	C	0.00000000	1.28276200	0.00000000
N	-1.16221600	0.62683300	0.00000000	N	-1.15635300	0.62418600	0.00000000
H	-2.02636700	-1.25132200	0.00000000	H	-2.02205400	-1.24756700	0.00000000
H	2.16663600	1.19445000	0.00000000	H	2.16284000	1.19419200	0.00000000
H	-0.06042000	2.37165200	0.00000000	H	-0.05859100	2.36802200	0.00000000

5-Dehydropyrimidine **1c**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
C	0.00000000	0.00000000	-1.23773200	C	0.00000000	0.00000000	-1.23130000
N	0.00000000	1.19413200	-0.64975900	N	0.00000000	1.19011100	-0.64694800
C	0.00000000	1.19833600	0.69283500	C	0.00000000	1.19115400	0.68774600
C	0.00000000	0.00000000	1.35891700	C	0.00000000	0.00000000	1.35594200
C	0.00000000	-1.19833600	0.69283500	C	0.00000000	-1.19115400	0.68774600
N	0.00000000	-1.19413200	-0.64975900	N	0.00000000	-1.19011100	-0.64694800
H	0.00000000	2.16097900	1.18864400	H	0.00000000	2.15449800	1.18701300
H	0.00000000	0.00000000	-2.32180100	H	0.00000000	0.00000000	-2.31755700
H	0.00000000	-2.16097900	1.18864400	H	0.00000000	-2.15449800	1.18701300

Pyridazine **2**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
N	0.00000000	0.66433900	-1.22561300	N	0.00000000	0.66105200	-1.22070000
C	0.00000000	1.31867500	-0.06745600	C	0.00000000	1.31195800	-0.06849100
C	0.00000000	0.68883500	1.17430500	C	0.00000000	0.68549000	1.17005200
C	0.00000000	-0.68883500	1.17430500	C	0.00000000	-0.68549000	1.17005200
C	0.00000000	-1.31867500	-0.06745600	C	0.00000000	-1.31195800	-0.06849100
N	0.00000000	-0.66433900	-1.22561300	N	0.00000000	-0.66105200	-1.22070000
H	0.00000000	1.26550100	2.08907100	H	0.00000000	1.26244500	2.08505300
H	0.00000000	2.39836800	-0.15087500	H	0.00000000	2.39307700	-0.14952500
H	0.00000000	-1.26550100	2.08907100	H	0.00000000	-1.26244500	2.08505300
H	0.00000000	-2.39836800	-0.15087500	H	0.00000000	-2.39307700	-0.14952500

2-Dehydropyridazine **2a**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
N	-1.23989000	-0.64640600	0.00000000	N	-1.24242400	-0.64384600	0.00000000
C	-0.17312800	-1.33376700	0.00000000	C	-0.17145300	-1.32361000	0.00000000
C	1.13046900	-0.84452100	0.00000000	C	1.12772200	-0.84046600	0.00000000
C	1.20139900	0.53177300	0.00000000	C	1.19886100	0.52874900	0.00000000
C	0.00000000	1.25656600	0.00000000	C	0.00000000	1.24885300	0.00000000
N	-1.20462500	0.70795700	0.00000000	N	-1.19863200	0.70311100	0.00000000
H	2.00242100	-1.48184300	0.00000000	H	1.99999800	-1.47867600	0.00000000
H	2.15103200	1.05114700	0.00000000	H	2.14818100	1.04962100	0.00000000
H	0.00570800	2.33953400	0.00000000	H	0.00843500	2.33304500	0.00000000

3-Dehydropyridazine **2b**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
N	-1.17217900	0.66501600	0.00000000	N	-1.16889400	-0.66720700	0.00000000
C	-0.02707600	1.37853400	0.00000000	C	-0.02842400	-1.37066100	0.00000000
C	1.17681000	0.71944800	0.00000000	C	1.17060700	-0.71211300	0.00000000
C	1.23945400	-0.63992700	0.00000000	C	1.23735200	0.64010500	0.00000000
C	0.00000000	-1.29726400	0.00000000	C	0.00000000	1.28915000	0.00000000
N	-1.15417800	-0.64117900	0.00000000	N	-1.14977900	0.63736100	0.00000000
H	2.16242800	-1.20513300	0.00000000	H	2.16123800	1.20503700	0.00000000
H	-0.06572500	-2.37861200	0.00000000	H	-0.06632800	2.37188400	0.00000000
H	-0.14733500	2.45214000	0.00000000	H	-0.14141000	-2.44688300	0.00000000

Pyrazine **3**

(U)B3LYP/cc-pVTZ				(U)M06-2X/cc-pVTZ			
C	0.00000000	1.13000400	0.69544900	C	0.00000000	1.12496800	0.69296100
C	0.00000000	1.13000400	-0.69544900	C	0.00000000	1.12496800	-0.69296100
N	0.00000000	0.00000000	-1.40025900	N	0.00000000	0.00000000	-1.39317800
C	0.00000000	-1.13000400	-0.69544900	C	0.00000000	-1.12496800	-0.69296100
C	0.00000000	-1.13000400	0.69544900	C	0.00000000	-1.12496800	0.69296100
N	0.00000000	0.00000000	1.40025900	N	0.00000000	0.00000000	1.39317800
H	0.00000000	2.06047800	1.25141100	H	0.00000000	2.05804000	1.24739500
H	0.00000000	2.06047800	-1.25141100	H	0.00000000	2.05804000	-1.24739500
H	0.00000000	-2.06047800	-1.25141100	H	0.00000000	-2.05804000	-1.24739500
H	0.00000000	-2.06047800	1.25141100	H	0.00000000	-2.05804000	1.24739500

3-Dehydropyrazine **3a**

(U)B3LYP/cc-pVTZ			
C	0.00000000	-1.26452500	0.00000000
C	1.19656800	-0.56317600	0.00000000
N	1.16292100	0.77913000	0.00000000
C	0.02441100	1.36137700	0.00000000
C	-1.19589100	0.68247900	0.00000000
N	-1.18434800	-0.64751800	0.00000000
H	-0.00804700	-2.34763500	0.00000000
H	2.15972400	-1.05645200	0.00000000
H	-2.15221400	1.18588200	0.00000000

(U)M06-2X/cc-pVTZ			
C	0.00000000	1.25845400	0.00000000
C	-1.19119000	0.55793900	0.00000000
N	-1.16174700	-0.77818000	0.00000000
C	-0.02173100	-1.35325300	0.00000000
C	1.19255900	-0.67791500	0.00000000
N	1.17919600	0.64573600	0.00000000
H	0.00375600	2.34306700	0.00000000
H	-2.15400600	1.05522600	0.00000000
H	2.15027800	-1.18253300	0.00000000