Exploring the Role of Consecutive Addition of Nitrogen Atoms on Stability and Reactivity of Hydrogen Bonded Azine-Water Complexes

Neha Chopra,*† Geetanjali Chopra† and Damanjit Kaur,†

†Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India

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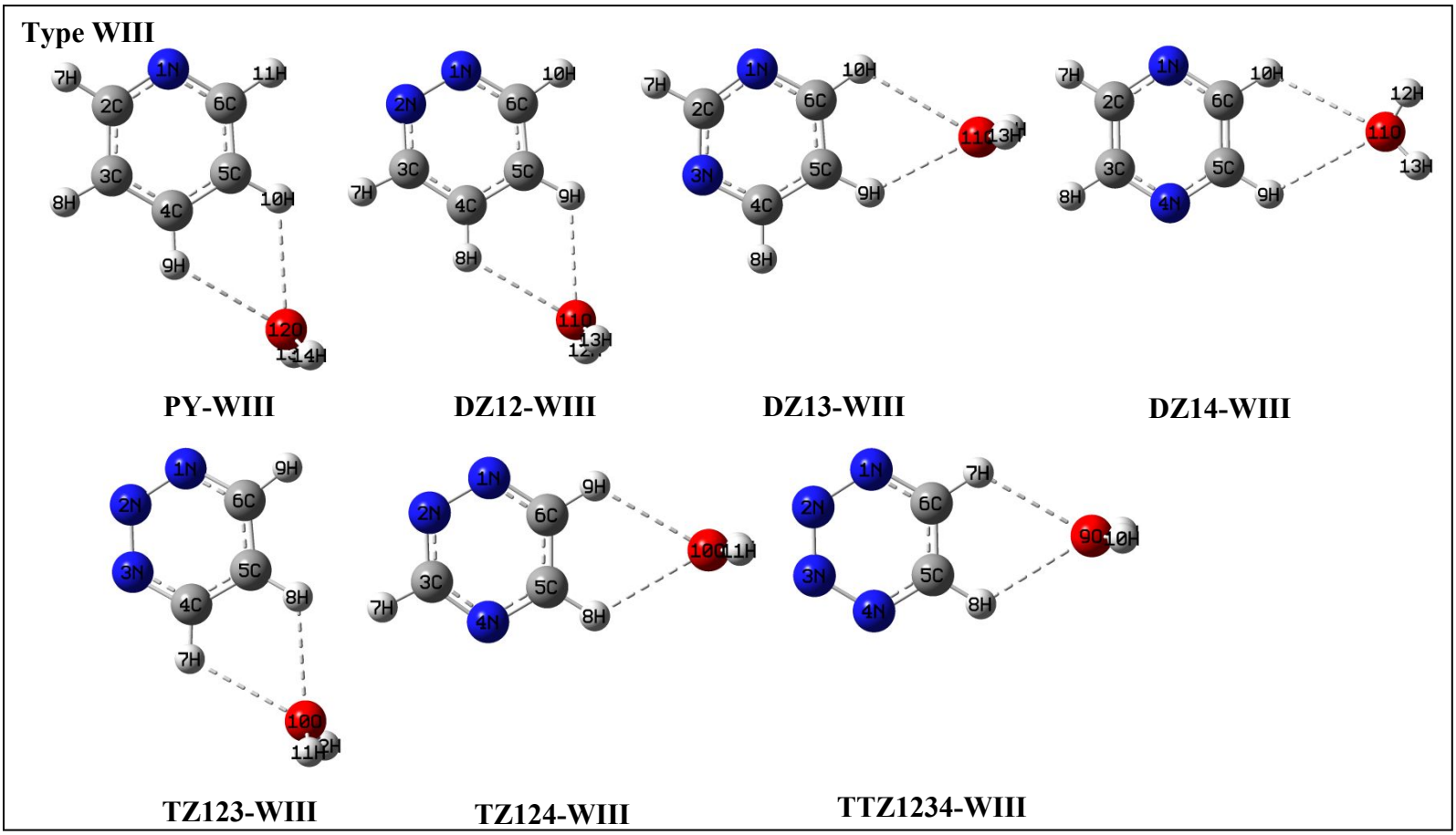
*****Corresponding E-mail address: nehaomnamah@gmail.com

Table S1: MEP parameters V_{max} (the most positive potential) and V_{min} (the most negative potential) of azines (in kcal/mol).

AZINES	V_{max}	V_{min}
PY	+25.28	-43.37
DZ12	+31.78	-41.46
DZ13	+27.76	-33.42
DZ14	+23.94	-30.70
TZ123	+38.42	-38.67
TZ124	+33.90	-35.11
TZ135	+27.42	-27.74
TTZ1234	+43.80	-32.29
TTZ1235	+35.87	-29.18
TTZ1245	+32.84	-24.39
PZ	+43.98	-24.32
HZ	+37.09	-11.62



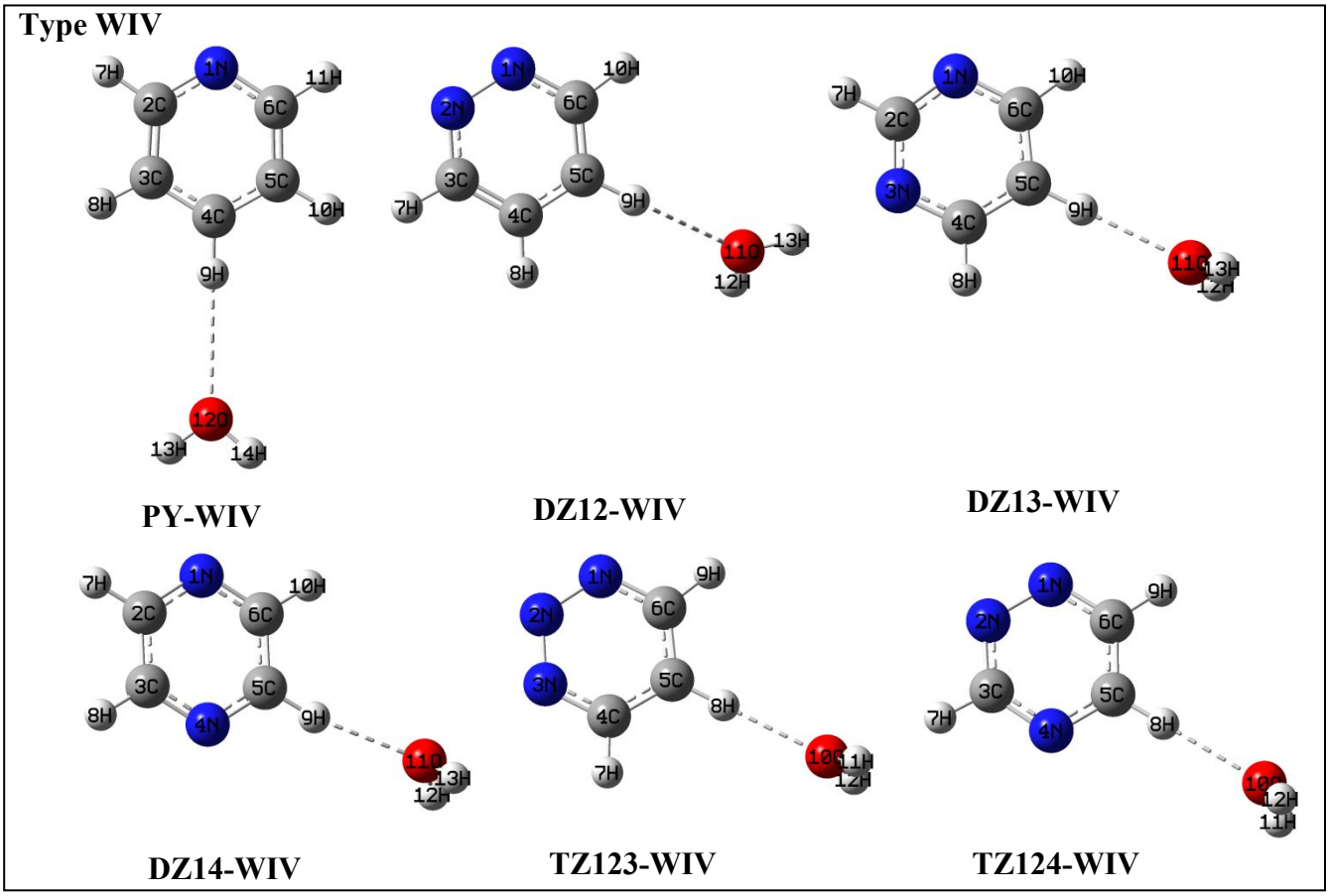


Figure S1: Optimized geometries of 1:1 hydrogen bonded complexes of azines with water at MP2/aug-cc-pVDZ level (type WIII & WIV).

Table S2: Second order delocalization energies $E^{(2)}$ (in kcal/mol) associated with orbital interactions at L1 and L2 levels, atomic charges (in au) and amount of charge transfer from azines to water (CT in e), MEP parameters V'_{min} and ΔV_{min} (in kcal/mol) in complexes of azine with water at L1 level.

Complexes	Orbital Interactions	$E^{(2)}$		Atomic Charges		CT	V'_{min}	ΔV_{min}
		L1	L2					
PY-WI	$n_{N1}\rightarrow\sigma^*_{O13\text{-}H12}$	14.12	12.35	$q_{N1}(q_{H12})$	-0.595(0.518)	+0.029	-14.10	+29.27
TZ123-WI	$^a n_{N2}\rightarrow n^*_{H10}$	**10.45**	**11.45**	$q_{N2}(q_{H10})$	-0.022(0.508)	+0.022	-14.62	+24.05
TTZ1234-WI	$n_{N3}\rightarrow\sigma^*_{O10\text{-}H9}$	6.46	4.73	$q_{N3}(q_{H9})$	-0.066(0.506)	+0.016	-9.89	+22.40
TTZ1235-WI	$n_{N2}\rightarrow\sigma^*_{O10\text{-}H9}$	6.69	4.96	$q_{N2}(q_{H9})$	-0.048(0.503)	+0.010	-9.45	+19.73
PZ-WI	$n_{N2}\rightarrow\sigma^*_{O9\text{-}H8}$	5.33	4.49	$q_{N2}(q_{H8})$	-0.046(0.500)	+0.008	-8.68	+15.64
HZ-WI	$n_{N4}\rightarrow\sigma^*_{O8\text{-}H7}$	2.74	1.89	$q_{N4}(q_{H10})$	-0.024(0.495)	+0.008	-5.59	+6.03
PY-WII	$n_{N1}\rightarrow\sigma^*_{O13\text{-}H12}$	11.62	11.44	$q_{N1}(q_{H12})$	-0.596(0.517)	+0.016	-21.71	+21.66
	$n_{(1)O13}\rightarrow\sigma^*_{C6\text{-}H11}$	0.11	0.12	$q_{O13}(q_{H11})$	-1.009(0.220)			
DZ12-WII	$n_{N1}\rightarrow\sigma^*_{O12\text{-}H11}$	10.66	10.32	$q_{N2}(q_{H11})$	-0.315(0.515)	+0.015	-19.86	+21.60
	$n_{(1)O12}\rightarrow\sigma^*_{C6\text{-}H10}$	0.20	0.19	$q_{O12}(q_{H10})$	-1.009(0.215)			
DZ13-WII	$n_{N1}\rightarrow\sigma^*_{O12\text{-}H11}$	9.36	8.33	$q_{N1}(q_{H11})$	-0.646(0.513)	+0.012	-13.59	+19.83
	$n_{(1)O12}\rightarrow\sigma^*_{C6\text{-}H10}$	0.22	0.21	$q_{O12}(q_{H9})$	-1.006(0.226)			
DZ14-WII	$^a n_{N1}\rightarrow n^*_{H11}$	**12.80**	**12.93**	$q_{N1}(q_{H11})$	-0.531(0.512)	+0.012	-10.80	+19.90
	$n_{(1)O13}\rightarrow\sigma^*_{C6\text{-}H11}$	0.19	0.20	$q_{O13}(q_{H11})$	-1.004(0.229)			
TZ123-WII	$^a n_{N1}\rightarrow n^*_{H10}$	**10.11**	**10.35**	$q_{N1}(q_{H10})$	-0.350(0.511)	+0.009	-35.96	+2.70
	$n_{(1)O11}\rightarrow\sigma^*_{C6\text{-}H9}$	0.46	0.39	$q_{O11}(q_{H9})$	-1.005(0.240)			
TZ124-WII	$n_{N1}\rightarrow\sigma^*_{O10\text{-}H11}$	8.30	7.39	$q_{N2}(q_{H10})$	-0.369(0.511)	+0.011	-19.16	+15.95
	$n_{(1)O11}\rightarrow\sigma^*_{C6\text{-}H9}$	0.23	0.22	$q_{O11}(q_{H9})$	-1.003(0.222)			
TZ135-WII	$n_{N1}\rightarrow\sigma^*_{O11\text{-}H10}$	6.87	6.99	$q_{N1}(q_{H10})$	-0.688(0.512)	+0.008	-7.83	+19.91
	$n_{(1)O11}\rightarrow\sigma^*_{C6\text{-}H9}$	0.33	0.31	$q_{O11}(q_{H9})$	-1.001(0.217)			
TTZ1234-WII	$n_{N1}\rightarrow\sigma^*_{O9\text{-}H10}$	4.38	4.73	$q_{N1}(q_{H10})$	-0.291(0.510)	+0.003	-31.58	+0.71
	$n_{(1)O9}\rightarrow\sigma^*_{C6\text{-}H7}$	1.10	0.41	$q_{O9}(q_{H7})$	-1.001(0.228)			
TTZ1245-WII	$n_{N1}\rightarrow\sigma^*_{O10\text{-}H9}$	4.80	4.94	$q_{N1}(q_{H9})$	-0.283(0.507)	+0.004	-20.10	+4.29
	$n_{(1)O10}\rightarrow\sigma^*_{C6\text{-}H8}$	0.69	0.49	$q_{O10}(q_{H8})$	-0.998(0.236)			
TTZ1235-WII	$n_{N1}\rightarrow\sigma^*_{O10\text{-}H9}$	4.99	5.18	$q_{N1}(q_{H9})$	-0.399(0.510)	+0.005	-27.10	+2.10
	$n_{(1)O10}\rightarrow\sigma^*_{C6\text{-}H8}$	0.65	0.30	$q_{O10}(q_{H8})$	-1.000(0.231)			
PZ-WII	$n_{N1}\rightarrow\sigma^*_{O9\text{-}H8}$	2.14	2.37	$q_{N1}(q_{H8})$	-0.320(0.504)	+0.003	-23.97	+0.35
	$n_{(1)O9}\rightarrow\sigma^*_{C6\text{-}H7}$	1.29	0.84	$q_{O9}(q_{H7})$	-0.995(0.244)			
PY-WIII	$n_{(1)O12}\rightarrow\sigma^*_{C4\text{-}H9}$	0.50	0.52	$q_{O12}(q_{H9})$	-0.970(0.234)	-0.005	-47.93	-4.56
	$n_{(2)O12}\rightarrow\sigma^*_{C4\text{-}H9}$	0.31	0.28					
	$n_{(1)O12}\rightarrow\sigma^*_{C5\text{-}H10}$	0.48	0.49	$q_{O12}(q_{H10})$	-0.970(0.234)			
	$n_{(2)O12}\rightarrow\sigma^*_{C5\text{-}H10}$	0.32	0.29					
DZ12-WIII	$n_{(1)O11}\rightarrow\sigma^*_{C4\text{-}H8}$	0.34	0.33	$q_{O11}(q_{H8})$	-0.974(0.242)	-0.005	-45.98	-4.46
	$n_{(2)O11}\rightarrow\sigma^*_{C4\text{-}H8}$	0.42	0.45					
	$n_{(1)O11}\rightarrow\sigma^*_{C5\text{-}H9}$	0.36	0.38	$q_{O11}(q_{H9})$	-0.974(0.242)			
	$n_{(2)O11}\rightarrow\sigma^*_{C5\text{-}H9}$	0.51	0.50					
DZ13-WIII	$n_{(1)O11}\rightarrow\sigma^*_{C5\text{-}H9}$	1.29	0.20	$q_{O11}(q_{H9})$	-0.972(0.248)	-0.005	-37.62	-4.20
	$n_{(2)O11}\rightarrow\sigma^*_{C5\text{-}H9}$	0.31	1.20					
	$n_{(1)O12}\rightarrow\sigma^*_{C6\text{-}H10}$	1.29	0.38	$q_{O12}(q_{H10})$	-1.006(0.226)			
	$n_{(2)O12}\rightarrow\sigma^*_{C6\text{-}H10}$	0.31	0.29					
DZ14-WIII	$n_{(1)O11}\rightarrow\sigma^*_{C2\text{-}H7}$	0.38	0.35	$q_{O11}(q_{H7})$	-0.977(0.220)	-0.005	-35.67	-4.97
	$n_{(2)O11}\rightarrow\sigma^*_{C2\text{-}H7}$	0.62	0.60					
	$n_{(1)O11}\rightarrow\sigma^*_{C3\text{-}H8}$	0.48	0.41	$q_{O11}(q_{H8})$	-0.977(0.220)			
	$n_{(2)O11}\rightarrow\sigma^*_{C3\text{-}H8}$	0.64	0.59					
TZ123-WIII	$n_{(1)O10}\rightarrow\sigma^*_{C4\text{-}H7}$	0.11	0.05	$q_{O10}(q_{H7})$	-0.977(0.227)	-0.005	-39.82	-1.15
	$n_{(2)O10}\rightarrow\sigma^*_{C4\text{-}H7}$	0.52	0.50					
	$n_{(1)O10}\rightarrow\sigma^*_{C5\text{-}H8}$	0.85	0.78	$q_{O10}(q_{H8})$	-0.977(0.253)			
	$n_{(2)O10}\rightarrow\sigma^*_{C5\text{-}H8}$	0.52	0.50					
TZ124-WIII	$n_{(1)O10}\rightarrow\sigma^*_{C5\text{-}H8}$	0.22	0.23	$q_{O10}(q_{H8})$	-0.976(0.227)	-0.005	-38.01	-2.90
	$n_{(2)O10}\rightarrow\sigma^*_{C5\text{-}H8}$	0.68	0.62					
	$n_{(1)O10}\rightarrow\sigma^*_{C6\text{-}H9}$	0.59	0.55	$q_{O10}(q_{H9})$	-0.976(0.231)			
	$n_{(2)O10}\rightarrow\sigma^*_{C6\text{-}H9}$	0.49	0.45					
TTZ1234-WIII	$n_{(1)O9}\rightarrow\sigma^*_{C5\text{-}H8}$	0.40	0.38	$q_{O9}(q_{H8})$	-0.981(0.237)	-0.006	-37.27	-4.98
	$n_{(2)O9}\rightarrow\sigma^*_{C5\text{-}H8}$	0.63	0.59					

	$n_{(1)O9}\rightarrow\sigma^{*}_{C6-H7}$	0.48	0.42	$q_{O9}(q_{H7})$	-0.981(0.237)			
	$n_{(2)O9}\rightarrow\sigma^{*}_{C6-H7}$	0.59	0.53					
PY-WIV	$n_{(1)O12}\rightarrow\sigma^{*}_{C4-H9}$	4.45	4.32	$q_{O12}(q_{H9})$	-0.974(0.243)	-0.007	-46.62	-3.25
DZ12–WIV	$n_{(1)O11}\rightarrow\sigma^{*}_{C5-H9}$	5.95	5.60	$q_{O11}(q_{H9})$	-1.020(0.253)	-0.009	-45.84	-4.38
DZ13-WIV	$n_{(1)O11}\rightarrow\sigma^{*}_{C5-H9}$	5.87	5.44	$q_{O11}(q_{H9})$	-1.010(0.248)	-0.008	-39.84	-6.42
DZ14-WIV	$n_{(1)O11}\rightarrow\sigma^{*}_{C5-H9}$	5.78	5.36	$q_{O11}(q_{H9})$	-1.005(0.263)	-0.008	-37.20	-6.50
TZ123-WIV	$n_{(1)O10}\rightarrow\sigma^{*}_{C5-H8}$	6.71	6.42	$q_{O10}(q_{H8})$	-1.014(0.288)	-0.010	-45.84	-7.17
TZ124-WIV	$n_{(1)O10}\rightarrow\sigma^{*}_{C5-H8}$	6.80	5.52	$q_{O10}(q_{H8})$	-1.011(0.271)	-0.010	-42.03	-6.92

[a] The orbital interaction $n_N\rightarrow n^{*}_H$ indicate the transfer of lone pair electrons on nitrogen atom to hydrogen atom in the complexes.

S1. Charge transfer and atomic charge analysis

NBO has been used to quantify the extent of charge transfer that is being transferred from one monomeric unit to another during the formation of complex. Table S2 illustrates the values of charge transfer (CT) from azines to water for the complexes under study at wB97XD/aug-cc-pVDZ level. The CT in **WI** complexes is from azine to water as indicated by positive CT values. The CT values of **WII** complexes involve HBs with both azine and water acting as HB donor as well as acceptor, therefore CT occurs from azine to water and vice-versa. The CT values of these complexes being positive indicate that CT from azine to water is higher than that from water to azine, so the direction of net CT is from azine to water. The CT is indicated to be the highest in type **WI** complexes followed by type **WII** complexes. The magnitude of CT in type **WI** and **WII** complexes decreases with increase in the number of N atoms in the ring. The magnitude of CT in type **WIII** and **WIV** complexes is from water to azine as suggested by their negative CT values. The CT in type **WIII** complexes is significantly lower in comparison to that in type **WIV** complexes despite the fact that there are two C-H$\cdots$O$_W$ interactions in former complexes whereas in case of type **WIV** complexes there is only single C-H$\cdots$O$_W$ interaction. The reason for such observation is explored on the basis of contraction of C-H bond of azines. In type **WIII** complexes, both the C-H bonds of azine are contracted but this contraction is considerably smaller than that occurring in type **WIV** complexes. Thus higher CT in type **WIV** complexes is consistent with larger contraction of C-H occurred during complex formation. The variation of CT in type **WIV** complexes suggests that it is favored by increase in number of N atoms.

NBO analysis is a reliable tool to derive information about the atomic charges which reflect the relative importance of electrostatic interactions associated with the complexes. The values of atomic charges of atoms forming HB evaluated at L1 level utilizing NBO analysis are presented in table S2. The atomic charges reflect that hydrogen nuclei forming HBs are deshielded upon HB formation. A large variation (-0.022 to -0.688 au) is observed in the atomic

charge values of azine nitrogen atoms that are involved in complex formation. In spite of low polarity of C-H bond, electrostatic interaction play a significant role in the unconventional C-H···O_w HB interaction as there is high electron density present on the oxygen atom (-0.974 to -1.009 au).

S2. Description of topological parameters

AIM provides an elegant approach to study the concept of hydrogen bonding interactions. Topologically stable critical points available in the complexes are designated as (3, -1) called bond critical points (bcps) and (3, +1) called ring critical points (rcps). The topological parameters such as electron density (ρ_c), its Laplacian ($\nabla^2\rho_c$), the total electron energy density (H_c) and its two components potential electron energy density (V_c) and kinetic electron energy density (G_c), calculated at the (3, -1) and (3, +1) critical points, are summarized in table S3. The values of the Laplacian $\nabla^2\rho_c$, the energy density H_c, and the balance between the kinetic electron energy density and the potential electron energy density $-G_c/V_c$ display the nature of the interaction. $\nabla^2\rho_c > 0$ indicates the interaction is of closed-shell type (ionic interaction, van der Waals forces or HBs).[1, 2] $\nabla^2\rho_c < 0$ implies that there is a shared interaction as in a covalent bond. The positive $\nabla^2\rho_c$ and the negative H_c mean that the interaction is partly covalent in nature. The values of $-G_c/V_c$ also reveal information about the nature of the bonding interaction. If $-G_c/V_c > 1$, then the interaction is noncovalent; if $-G_c/V_c$ value ranges between 0.5 and 1, then the interaction is partly covalent in nature.[3]

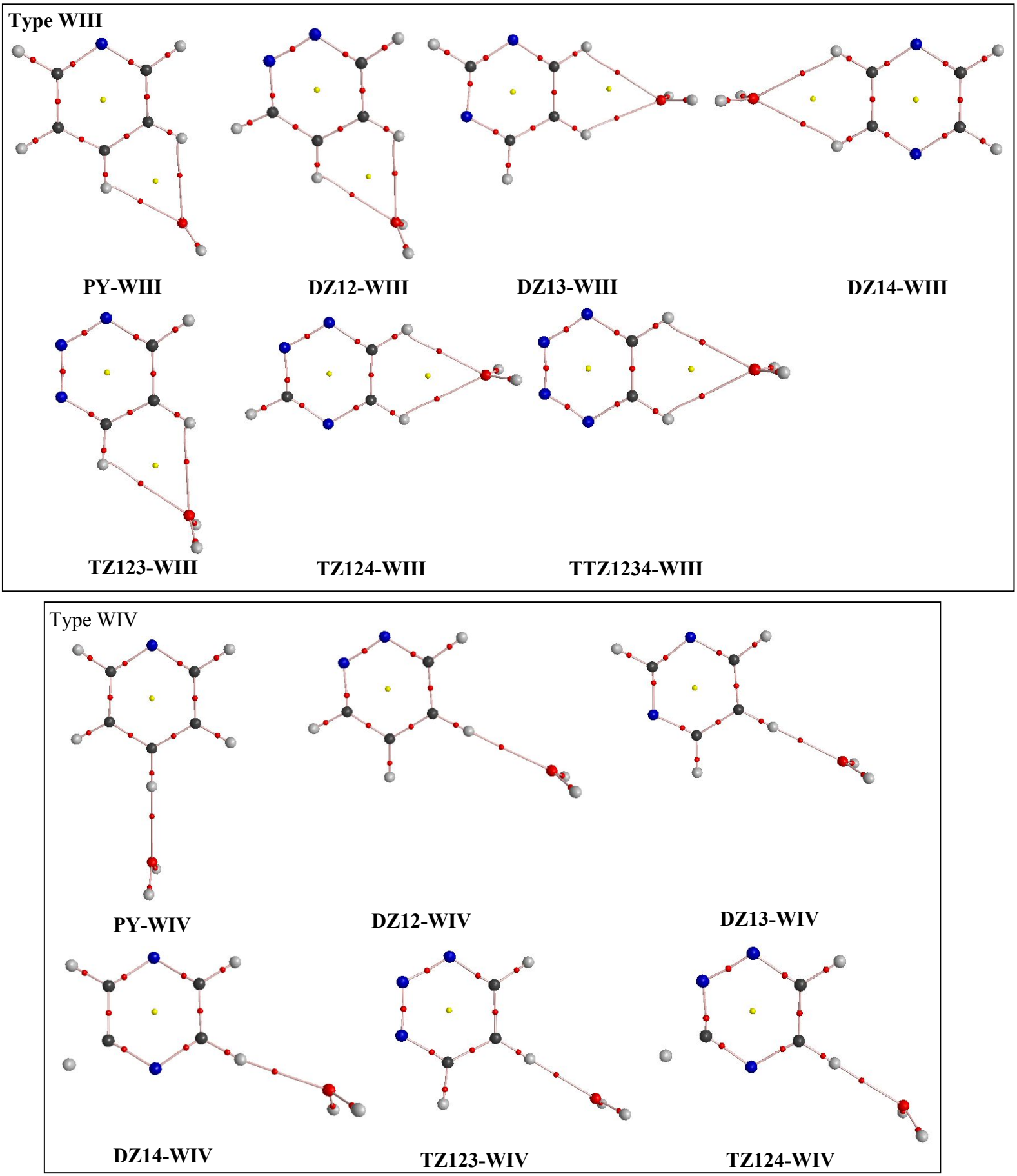


Figure S2: AIM molecular graphs of complexes of azines with water at MP2/aug-cc-pVDZ level (Type WIII & WIV). Small red balls indicate bond critical points and small yellow balls indicate ring critical points.

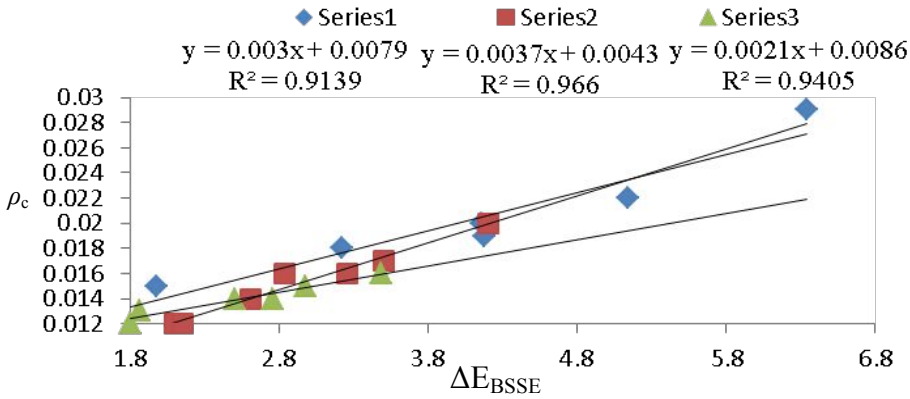


Figure S3: A plot of the relation between stabilization energy (ΔE_{BSSE} in kcal/mol) and ρ_c (au) at MP2/aug-cc-pVDZ level.

series 1 implies the complexes involving single N···H-O_W HB interaction.
series 2 implies the complexes involving two HBs C-H···O_w forming bifurcated structure.
series 3 results from single C-H···O_w hydrogen bonded complexes.

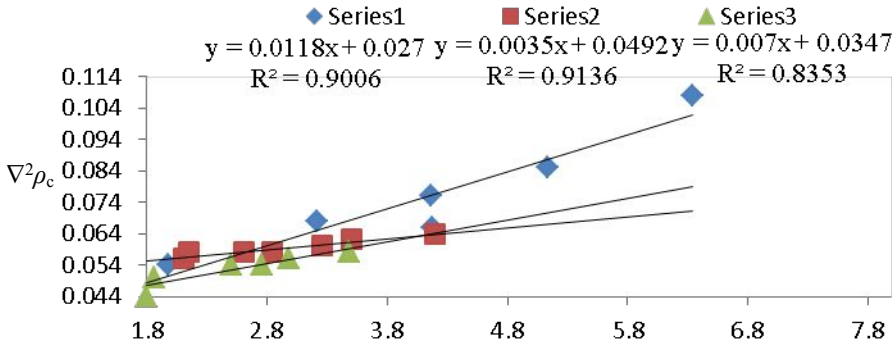


Figure S4: A plot of the relation between stabilization energy (ΔE_{BSSE} in kcal/mol) and $\nabla^2\rho c$ (au) at MP2/aug-cc-pVDZ level.

series 1 implies the complexes involving single N···H-O_W HB interaction.
series 2 implies the complexes involving two HBs C-H···O_w forming bifurcated structure.
series 3 results from single C-H···O_w hydrogen bonded complexes.

Table S3: The topological and energetic properties at the bond critical points (bcps) and the ring critical points (rcps) for the complexes of azines with water evaluated at MP2/aug-cc-pVDZ level. (All the values are in au)

COMPLEXES	HBs	CP	ρ_c	$\nabla^2_{\rho c}$	G_c	V_c	H_c	$-G_c/V_c$
PY-WI	H13···N1	(3, -1)	0.029	0.108	0.023	-0.020	-0.003	1.15
		(3, +1)	0.022	0.170	0.034	-0.026	-0.008	1.31
TZ123-WI	H10···N2	(3, -1)	0.022	0.085	0.018	-0.014	0.004	1.28
		(3, +1)	0.024	0.187	0.039	-0.030	0.009	1.30
TTZ1234-WI	H9···N3	(3, -1)	0.019	0.066	0.015	-0.012	0.003	1.25
		(3, +1)	0.025	0.196	0.040	-0.032	0.008	1.25
TTZ1235-WI	H9···N2	(3, -1)	0.020	0.076	0.016	-0.013	0.003	1.23
		(3, +1)	0.027	0.208	0.044	-0.036	0.008	1.22
PZ-WI	H8···N2	(3, -1)	0.018	0.068	0.014	-0.011	0.003	1.27
		(3, +1)	0.026	0.204	0.043	-0.034	0.009	1.26
HZ-WI	H7···N4	(3, -1)	0.015	0.054	0.011	-0.008	0.003	1.38
		(3, +1)	0.029	0.242	0.050	-0.040	0.010	1.25
PY-WII	H12···N1	(3, -1)	0.027	0.102	0.022	-0.019	0.003	1.15
		(3, +1)	0.022	0.170	0.034	-0.026	0.008	1.31
DZ12-WII	H11···N2	(3, -1)	0.026	0.100	0.022	-0.018	0.004	1.22
		(3, +1)	0.023	0.177	0.036	-0.028	0.008	1.29
DZ13-WII	H11···N1	(3, -1)	0.025	0.094	0.020	-0.017	0.003	1.18
		(3, +1)	0.025	0.186	0.038	-0.030	0.008	1.27
DZ14-WII	H11···N1	(3, -1)	0.025	0.093	0.020	-0.017	0.003	1.18
		(3, +1)	0.024	0.185	0.038	-0.030	0.008	1.27
TZ123-WII	H10···N1	(3, -1)	0.023	0.086	0.019	-0.016	0.003	1.19
	H9···O11	(3, -1)	0.008	0.039	0.008	-0.006	0.002	1.33
		(3, +1)	0.024	0.187	0.038	-0.030	0.008	1.27
		(3, +1)[a]	0.008	0.045	0.009	-0.007	0.002	1.29
TZ124-WII	H10···N1	(3, -1)	0.024	0.089	0.019	-0.016	0.003	1.19
	H9···O11	(3, -1)	0.008	0.039	0.008	-0.006	0.002	1.33
		(3, +1)	0.025	0.162	0.041	-0.033	0.008	1.24
		(3, +1)[a]	0.008	0.043	0.009	-0.006	0.003	1.50
TZ135-WII	H10···N1	(3, -1)	0.022	0.081	0.018	-0.015	0.003	1.20
		(3, +1)	0.028	0.205	0.043	-0.035	0.008	1.23
TTZ1234-WII	H10···N1	(3, -1)	0.019	0.071	0.016	-0.014	0.002	1.14
	H8···O11	(3, -1)	0.007	0.037	0.010	-0.009	0.001	1.11
		(3, +1)	0.025	0.195	0.040	-0.032	0.008	1.25
		(3, +1)[a]	0.009	0.055	0.011	-0.008	0.003	1.38
TTZ1245-WII	H10···N1	(3, -1)	0.020	0.073	0.016	-0.014	0.002	1.14
	H8···O9	(3, -1)	0.008	0.038	0.008	-0.007	0.001	1.14
		(3, +1)	0.027	0.202	0.043	-0.035	0.008	1.23
		(3, +1)[a]	0.008	0.046	0.009	-0.007	0.002	1.29

TTZ1235-WII	H10···N4	(3, -1)	0.021	0.074	0.015	-0.014	0.001	1.07
	H8···O10	(3, -1)	0.008	0.037	0.008	-0.007	0.001	1.14
		(3, +1)	0.029	0.210	0.044	-0.036	0.008	1.22
		(3, +1)[a]	0.008	0.045	0.009	0.007	0.002	1.29
PZ-WII	H8···N1	(3, -1)	0.015	0.055	0.013	-0.012	0.001	1.08
	H7···O9	(3, -1)	0.011	0.044	0.010	-0.009	0.001	1.11
		(3, +1)	0.026	0.206	0.043	-0.034	0.009	1.26
		(3, +1)[a]	0.008	0.049	0.010	-0.007	0.003	1.43
PY-WIII	H9···O12	(3, -1)	0.006	0.028	0.006	-0.005	0.001	1.20
	H10···O12	(3, -1)	0.006	0.028	0.006	-0.005	0.001	1.20
		(3, +1)	0.022	0.170	0.034	-0.026	0.008	1.31
		(3, +1)[a]	0.005	0.024	0.004	-0.003	0.001	1.33
DZ12-WIII	H8···O11	(3, -1)	0.008	0.029	0.006	-0.005	0.001	1.20
	H9···O11	(3, -1)	0.008	0.029	0.006	-0.005	0.001	1.20
		(3, +1)	0.023	0.177	0.036	-0.028	0.008	1.29
		(3, +1)[a]	0.005	0.026	0.005	-0.004	0.001	1.25
DZ13-WIII	H9···O11	(3, -1)	0.007	0.029	0.006	-0.005	0.001	1.20
	H10···O11	(3,-1)	0.007	0.029	0.006	-0.005	0.001	1.20
		(3, +1)	0.025	0.186	0.039	-0.031	0.008	1.26
		(3, +1)[a]	0.004	0.024	0.005	-0.003	0.002	1.66
DZ14-WIII	H7···O11	(3, -1)	0.006	0.029	0.006	-0.005	0.001	1.20
	H8···O11	(3, -1)	0.006	0.029	0.006	-0.005	0.001	1.20
		(3, +1)	0.025	0.190	0.040	-0.031	0.009	1.29
		(3, +1)[a]	0.005	0.028	0.005	-0.004	0.001	1.25
TZ123-WIII	H9···O10	(3, -1)	0.009	0.031	0.006	-0.005	0.001	1.20
	H8···O10	(3, -1)	0.008	0.031	0.008	-0.007	0.001	1.14
		(3, +1)	0.024	0.187	0.038	-0.030	0.008	1.27
		(3, +1)[a]	0.005	0.028	0.005	-0.004	0.001	1.25
TZ124-WIII	H9···O10	(3, -1)	0.008	0.030	0.007	-0.006	0.001	1.17
	H8···O10	(3, -1)	0.008	0.030	0.007	-0.006	0.001	1.17
		(3, +1)	0.026	0.194	0.041	-0.033	0.008	1.24
		(3, +1)[a]	0.005	0.028	0.005	-0.004	0.001	1.25
TTZ1234-WIII	H7···O9	(3, -1)	0.010	0.032	0.007	-0.006	0.001	1.17
	H8···O9	(3, -1)	0.010	0.032	0.007	-0.006	0.001	1.17
		(3, +1)	0.025	0.195	0.040	-0.032	0.008	1.25
		(3, +1)[a]	0.006	0.030	0.006	-0.004	0.002	1.50
PY-WIV	H9···O12	(3, -1)	0.012	0.044	0.010	-0.009	0.001	1.11
		(3, +1)	0.022	0.174	0.035	-0.026	0.009	1.35
DZ12–WIV	H9···O11	(3, -1)	0.014	0.054	0.013	-0.010	0.003	1.30
		(3, +1)	0.023	0.177	0.036	-0.028	0.008	1.29

DZ13-WIV	H9···O11	(3, -1)	0.014	0.054	0.013	-0.012	0.001	1.08
		(3, +1)	0.024	0.186	0.038	-0.030	0.008	1.27
DZ14-WIV	H9···O11	(3, -1)	0.013	0.051	0.012	-0.012	0.000	1.00
		(3, +1)	0.024	0.185	0.038	-0.030	0.008	1.27
TZ123-WIV	H8···O10	(3, -1)	0.016	0.058	0.014	-0.013	0.001	1.08
		(3, +1)	0.024	0.187	0.038	-0.030	0.008	1.27
TZ124-WIV	H8···O10	(3, -1)	0.015	0.056	0.014	-0.013	0.001	1.08
		(3, +1)	0.026	0.194	0.041	-0.033	0.008	1.24

(3, -1) indicate bcps; (3, +1)[a] indicate rcps in azines; (3, +1) indicate rcps in pseudo five-membered ring.

S3. Analysis of V_{max} and V_{min}

The study of molecular electrostatic potential (MEP) focuses to interpret and predict the electrophilic and nucleophilic regions present in the molecule. The high negative electrostatic potential associated with ring nitrogens makes these sites in azines attractive for electrophiles. The magnitude of V_{min} is found to be decreased with increase in the number of nitrogens in the ring which points to the fact that conclude that nitrogen atoms compete for polarizable electronic charge, each get a small proportion of it (table S1). The strong positive electrostatic potential V_{max} along the C-H bond vector of azine make these sites attractive for nucleophiles. The magnitude of V_{max} is found to be increased with increase in the number of nitrogens in the ring (table S1). Higher V_{min} and V_{max} values are associated with DZ12, TZ123, TTZ1234 isomeric forms in which ring nitrogens are adjacent to each other.

It is to be anticipated from the most negative potential values of complexes, V'_{min} (table S2) that upon complexation with water there is large decrease in negative lone pair potentials of ring nitrogen atoms in case of complexes involving single N···H-O_W interaction whereas there is increase in the negative lone pair potential of ring nitrogens in case of complexes involving single C-H···O_W interaction. The type **WI** and **WII** complexes have positive value of ΔV_{min} which indicates that the amount of negative lone pair is transferred from azine ring to water during the formation of complex. The type **WI** complexes involving single N···H-O_W interaction have larger value of ΔV_{min} in relative to respective type **WII** complexes involving with N···H-O_W and C-H···O_w interactions. The type **WIII** and **WIV** complexes have negative value of ΔV_{min} which indicates the gain in negative lone pair potential by azine at the expense of water molecule during the formation of complex. The type **WIV** complexes with direct C-H···O_w bonds have larger value of ΔV_{min} in comparison to type **WIII** complexes involving bifurcated structure with oxygen of water connected to two C-H hydrogens.

Table S4: SAPT components (in kcal/mol) of the stabilization energy for complexes of azines with water evaluated at L2 level.

Complexes	E_{els}	E_{ind}	E_{disp}	E_{exc}	$\delta E^{HF}_{int,r}$	E_{int}
PY-WI	-13.90	-5.72	-4.98	19.86	-1.56	-6.30
TZ123-WI	-14.10	-5.80	-5.01	20.98	-1.64	-5.57
TTZ1234-WI	-14.42	-5.98	-5.08	22.74	-1.75	-4.49
TTZ1235-WI	-14.38	-5.92	-5.04	22.68	-1.79	-4.45
PZ-WI	-14.62	-6.01	-5.12	23.55	-1.72	-3.92
HZ-WI	-14.92	-6.08	-5.18	25.02	-1.82	-2.98
PY-WII	-12.68	-5.29	-4.32	17.08	-1.39	-6.60
DZ12–WII	-13.62	-5.48	-4.72	18.78	-1.45	-6.49
DZ13-WII	-13.78	-5.62	-4.85	19.88	-1.52	-5.89
DZ14-WII	-13.92	-5.72	-4.92	20.48	-1.58	-5.66
TZ123-WII	-14.72	-6.05	-5.24	21.58	-1.78	-6.21
TZ124-WII	-14.56	-5.95	-5.12	21.35	-1.75	-6.03
TZ135-WII	-14.02	-5.58	-4.88	20.75	-1.48	-5.21
TTZ1234-WII	-15.01	-6.10	-5.35	22.85	-1.80	-5.41
TTZ1245-WII	-14.94	-5.90	-5.15	22.54	-1.71	-5.16
TTZ1235-WII	-14.99	-6.04	-5.28	22.73	-1.67	-5.25
PZ-WII	-15.14	-6.13	-5.42	23.54	-1.86	-5.01
PY-WIII	-8.40	-1.92	-2.10	10.65	-0.26	-2.03
DZ12–WIII	-8.98	-2.05	-2.24	11.05	-0.40	-2.62
DZ13-WIII	-8.68	-2.08	-2.20	11.10	-0.32	-2.18
DZ14-WIII	-8.42	-2.02	-2.18	10.98	-0.28	-1.92
TZ123-WIII	-9.50	-2.22	-2.42	11.25	-0.68	-3.57
TZ124-WIII	-9.02	-2.15	-2.36	11.18	-0.58	-2.93
TTZ1234-WIII	-9.68	-2.26	-2.45	11.45	-0.75	-3.69
PY-WIV	-8.10	-1.88	-2.25	10.38	-0.12	-1.97
DZ12–WIV	-8.68	-2.10	-2.30	10.44	-0.28	-2.92
DZ13-WIV	-8.50	-2.05	-2.27	10.20	-0.20	-2.82
DZ14-WIV	-8.25	-1.98	-2.28	10.50	-0.25	-2.26
TZ123-WIV	-8.98	-2.30	-2.51	11.00	-0.68	-3.47
TZ124-WIV	-8.60	-2.04	-2.45	10.58	-0.30	-2.81

Table S5: Geometrical parameters of WI complexes of PY and TZ123 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	PY-WI		Parameters	TZ123-WI	
	L1	L2		L1	L2
C2-N1	1.341	1.352	N2-N1	1.323	1.341
C3-C2	1.397	1.405	N3-N2	1.324	1.343
C4-C3	1.396	1.405	C4-N3	1.342	1.352
C5-C4	1.396	1.405	C5-C4	1.389	1.398
C6-N1	1.341	1.352	C6-N1	1.342	1.353
H7-C2	1.092	1.095	H7-C4	1.091	1.093
H8-C3	1.090	1.093	H8-C5	1.090	1.092
H9-C4	1.091	1.094	H9-C6	1.091	1.093
H10-C5	1.090	1.093	H10-N2	2.028	2.017
H11-C6	1.092	1.095	O11-H10	0.974	0.975
O12-C13	0.981	0.980	H12-O11	0.964	0.965
H13-N1	1.919	1.915	N3-N2-N1	122.27	122.09
H14-O12	0.964	0.965	C4-N3-N2	119.44	119.31
C3-C2-N1	123.17	123.23	C5-C4-N3	121.86	121.92
C4-C3-C2	118.53	118.77	C6-N1-N2	119.44	119.25
C5-C4-C3	118.65	118.38	H7-C4-N3	115.48	115.31
C6-N1-C2	31.03	117.62	H8-C5-C4	122.43	122.28
H7-C2-N1	116.12	115.92	H9-C6-N1	115.42	115.23
H8-C3-C2	120.14	120.00	H10-N2-N1	120.92	125.16
H9-C4-C3	120.67	120.81	O11-H10-N2	145.81	146.83
H10-C5-C4	121.33	121.23	H12-O11-H10	104.48	103.52
H11-C6-N1	116.14	115.92	C4-N3-N2-N1	0.0	0.0
O12-H13-N1	176.85	176.50	C5-C4-N3-N2	-0.0	0.0
H13-N1-C2	121.21	121.29	C6-N1-N2-N3	-0.0	-0.0
H14-O12-H13	104.98	104.16	H7-C4-N3-N2	180.0	180.0
C4-C3-C2-N1	-0.1	-0.1	H8-C5-C4-N3	180.0	180.0
C5-C4-C3-C2	-0.0	-0.0	H9-C6-N1-N2	-180.0	-180.0
C6-N1-C2-C3	0.2	0.2	H10-N2-N1-C6	179.9	179.4
H7-C2-N1-C3	-180.0	-180.0	O11-H10-N2-N1	-174.1	-168.5
H8-C3-C2-N1	-180.0	-180.0	H12-O11-H10-N2	-6.6	-12.1
H9-C4-C3-C2	-180.0	-180.0			
H10-C5-C4-C3	-179.9	-179.9			
H11-C6-N1-C2	179.7	179.7			
O12-H13-N1-C2	-89.0	-89.8			
H13-N1-C2-C3	176.1	176.1			
H14-O12-H13-N1	-178.5	-177.7			

Table S6: Geometrical parameters of WI complexes of TTZ1234 and TTZ1235 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TTZ1234-WI		Parameters	TTZ1235-WI	
	L1	L2		L1	L2
N2-N1	1.332	1.347	N2-N1	1.321	1.338
N3-N2	1.318	1.341	N3-N2	1.323	1.339
N4-N3	1.331	1.345	C4-N3	1.342	1.351
C5-N4	1.330	1.345	N5-C4	1.332	1.344
C6-N1	1.330	1.346	C6-N5	1.332	1.343
H7-C5	1.091	1.093	H7-C4	1.091	1.092
H8-C6	1.091	1.093	H8-C6	1.091	1.092
H9-N3	2.097	2.085	H9-N2	2.084	2.061
O10-H9	0.971	0.972	O10-H9	0.972	0.973
H11-O10	0.964	0.965	H11-O10	0.964	0.965
N3-N2-N1	121.53	121.51	N3-N2-N1	121.12	120.62
N4-N3-N2	122.36	122.48	C4-N3-N2	117.69	117.85
C5-N4-N3	117.85	117.30	N5-C4-N3	125.28	125.45
C6-N1-N2	118.13	117.66	C6-N5-C4	112.93	112.77
H7-C5-N4	116.85	116.34	H7-C4-N3	116.20	116.20
H8-C6-N1	116.86	116.35	H8-C6-N5	118.55	118.35
H9-N3-N2	116.41	112.60	H9-N2-N1	112.49	122.18
O10-H9-N3	140.41	139.86	O10-H9-N2	117.19	178.51
H11-O10-H9	104.55	103.66	H11-O10-H9	104.60	103.75
N4-N3-N2-N1	0.1	0.0	C4-N3-N2-N1	-0.0	0.0
C5-N4-N3-N2	-0.0	0.0	N5-C4-N3-N2	0.0	-0.0
C6-N1-N2-N3	-0.1	-0.1	C6-N5-C4-N3	-0.0	0.0
H7-C5-N4-N3	-180.0	180.0	H7-C4-N3-N2	-180.0	180.0
H8-C6-N1-N2	-180.0	-180.0	H8-C6-N5-C4	-180.0	180.0
H9-N3-N2-C1	179.7	179.7	H9-N2-N1-N3	-179.1	-180.0
O10-H9-N3-N2	-16.3	-19.5	O10-H9-N2-N1	162.6	179.1
H11-O10-H9-N3	16.6	20.3	H11-O10-H9-N2	16.6	0.6

Table S7: Geometrical parameters of WI complexes of PZ and HZ at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	PZ-WI		Parameters	HZ-WI	
	L1	L2		L1	L2
N2-N1	1.318	1.337	N2-N1	1.334	1.357
N3-N2	1.325	1.342	N3-N2	1.312	1.330
N4-N3	1.327	1.343	N4-N3	1.323	1.333
N5-N4	1.321	1.340	N5-N4	1.321	1.352
C6-N5	1.335	1.347	N6-N5	1.324	1.334
H7-C6	1.090	1.092	H7-N4	2.232	2.090
H8-N2	2.137	2.103	O8-H7	0.967	0.974
O9-H8	0.970	0.971	H9-O8	0.964	0.971
H10-O9	0.964	0.965	N3-N2-N1	116.07	113.70
N3-N2-N1	120.91	120.55	N4-N3-N2	121.04	122.14
N4-N3-N2	121.16	121.58	N5-N4-N3	116.33	114.23
N5-N4-N3	120.33	119.89	N6-N5-N4	115.84	113.28
N3-N2-N1	120.91	120.55	H7-N4-N3	120.53	123.97
N4-N3-N2	121.16	121.58	O8-H7-N4	130.70	132.70
N5-N4-N3	120.33	119.89	H9-O8-H7	105.12	105.36
C6-N5-N4	116.66	116.62	N4-N3-N2-N1	-16.4	-20.5
H7-C6-N5	117.71	117.42	N5-N4-N3-N2	-17.2	-20.4
H8-N2-N3	119.60	123.43	N6-N5-N4-N3	33.1	39.8
O9-H8-N2	174.39	171.13	H7-N4-N3-N2	158.1	158.0
H10-O9-H8	104.84	104.03	O8-H7-N4-N3	-82.0	-108.2
N4-N3-N2-N1	0.0	-0.0	H9-O8-H7-N4	177.1	-141.5
N5-N4-N3-N2	-0.0	0.0			
C6-N5-N4-N3	0.0	0.0			
H7-C6-N5-N4	180.0	180.0			
H8-N2-N3-N1	180.0	180.0			
O9-H8-N2-N3	180.0	180.0			
H10-O9-H8-N2	-180.0	-180.0			

Table S8: Geometrical parameters of WII complexes of PY and DZ12 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	PY-WII		Parameters	DZ12-WII	
	L1	L2		L1	L2
C2-N1	1.348	1.353	N2-N1	1.332	1.348
C3-C2	1.396	1.405	C3-N2	1.336	1.352
C4-C3	1.396	1.405	C4-C3	1.400	1.406
C5-C4	1.396	1.405	C5-C4	1.386	1.397
C6-N1	1.347	1.352	C6-N1	1.337	1.352
H7-C2	1.088	1.094	H7-C3	1.091	1.094
H8-C3	1.087	1.093	H8-C4	1.090	1.093
H9-C4	1.088	1.094	H9-C5	1.090	1.093
H1O-C5	1.087	1.093	H10-C6	1.091	1.093
H11-C6	1.088	1.094	H11-N2	1.939	1.952
H12-N1	1.972	1.938	O12-H11	0.979	0.978
O13-H12	0.983	0.979	H13-O12	0.963	0.964
H14-O13	0.971	0.964	C3-N2-N1	120.34	120.13
C3-C2-N1	123.17	123.20	C4-C3-N2	123.04	123.34
C4-C3-C2	118.76	118.83	C5-C4-C3	116.92	116.91
C5-C4-C3	118.59	118.34	C6-N1-N2	119.10	118.58
C6-N1-C2	117.52	117.56	H7-C3-N2	114.96	114.34
H7-C2-N1	115.63	115.65	H8-C4-C3	120.80	120.88
H8-C3-C2	120.02	119.95	H9-C5-C4	122.18	122.16
H9-C4-C3	120.71	120.84	H10-C6-N1	114.98	114.44
H1O-C5-C4	121.26	121.23	H11-N2-N1	129.14	137.95
H11-C6-N1	115.89	116.10	O12-H11-N2	160.81	150.36
H12-N1-C2	107.27	101.04	H13-O12-H11	105.27	104.71
O13-H12-N1	164.22	155.89	C4-C3-N2-N1	-0.0	-0.0
H14-O13-H12	105.80	104.71	C5-C4-C3-N2	0.0	0.0
C4-C3-C2-N1	-0.2	-0.0	C6-N1-N2-C3	-0.0	0.0
C5-C4-C3-C2	0.1	0.0	H7-C3-N2-N1	180.0	180.0
C6-N1-C2-C3	0.3	0.0	H8-C4-C3-N2	-180.0	-180.0
H7-C2-N1-C3	179.8	180.0	H9-C5-C4-C3	180.0	180.0
H8-C3-C2-N1	179.8	180.0	H10-C6-N1-N2	-180.0	-180.0
H9-C4-C3-C2	180.1	-180.0	H11-N2-N1-C6	179.4	179.8
H1O-C5-C4-C3	180.0	-180.0	O12-H11-N2-N1	-177.8	-179.6
H11-C6-N1-C2	179.9	180.0	H13-O12-H11-N2	177.9	178.7
H12-N1-C2-C3	-179.6	-179.9			
O13-H12-N1-C2	0.0	0.0			
H14-O13-H12-N1	179.7	-180.0			

Table S9: Geometrical parameters of WII complexes of DZ13 and DZ14 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	DZ13-WII		Parameters	DZ14-WII	
	L1	L2		L1	L2
C2-N1	1.349	1.349	C2-N1	1.339	1.352
N3-C2	1.337	1.348	C3-C2	1.400	1.406
C4-N3	1.340	1.351	N4-C3	1.338	1.351
C5-C4	1.400	1.403	C5-N4	1.338	1.351
C6-N1	1.341	1.352	C6-N1	1.338	1.351
H7-C2	1.091	1.093	H7-C2	1.091	1.094
H8-C4	1.093	1.095	H8-C3	1.091	1.094
H9-C5	1.089	1.092	H9-C5	1.092	1.094
H10-C6	1.092	1.094	H10-C6	1.092	1.094
H11-N1	1.966	1.975	H11-N1	1.972	1.977
O12-H11	0.977	0.976	O12-H11	0.977	0.976
H13-O12	0.963	0.965	H13-O12	0.963	0.965
N3-C2-N1	126.70	126.99	C3-C2-N1	121.55	121.84
C4-N3-C2	116.05	115.76	N4-C3-C2	122.07	122.50
C5-C4-N3	122.29	122.22	C5-N4-C3	116.16	115.35
C6-N1-C2	116.52	116.36	C6-N1-C2	116.56	115.90
H7-C2-N1	116.61	116.50	H7-C2-N1	117.01	116.59
H8-C4-N3	116.53	116.40	H8-C3-C2	120.67	120.65
H9-C5-C4	121.72	121.50	H9-C5-N4	117.30	116.88
H10-C6-N1	116.38	116.19	H10-C6-N1	117.38	117.05
H11-N1-C2	139.36	144.31	H11-N1-C2	104.14	99.39
O12-H11-N1	155.76	150.19	O12-H11-N1	156.04	150.02
H13-O12-H11	105.64	104.83	H13-O12-H11	105.65	104.76
C4-N3-C2-N1	-0.0	-0.0	N4-C3-C2-N1	0.0	-0.2
C5-C4-N3-C2	0.0	0.0	C5-N4-N3-C2	-0.0	0.1
C6-N1-C2-N3	0.0	-0.0	C6-N1-C2-C3	-0.0	0.2
H7-C2-N1-C6	-180.0	180.0	H7-C2-N1-C3	-180.0	-179.8
H8-C4-N3-C2	-180.0	-180.0	H8-C3-C2-N1	-180.0	179.9
H9-C5-C4-N3	180.0	180.0	H9-C5-N4-C3	180.1	-179.9
H10-C6-N1-C2	-180.0	-180.0	H10-C6-N1-C2	-180.0	-180.0
H11-N1-C2-N3	-179.8	-179.9	H11-N1-C2-C3	179.8	177.8
O12-H11-N1-C2	-179.8	179.7	O12-H11-N1-C2	-1.0	-4.5
H13-O12-H11-N1	-180.0	-179.1	H13-O12-H11-N1	-179.7	-173.4

Table S10: Geometrical parameters of WII complexes of TZ123 and TZ124 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TZ123-WII		Parameters	TZ124-WII	
	L1	L2		L1	L2
N2-N1	1.323	1.341	N2-N1	1.332	1.347
N3-N2	1.324	1.343	C3-N2	1.337	1.350
C4-N3	1.342	1.352	N4-C3	1.341	1.352
C5-C4	1.389	1.398	C5-N4	1.329	1.343
C6-N1	1.342	1.353	C6-N1	1.333	1.349
H7-C4	1.091	1.093	H7-C3	1.090	1.093
H8-C5	1.090	1.092	H8-C5	1.093	1.094
H9-C6	1.091	1.093	H9-C6	1.090	1.093
H10-N2	2.028	2.017	H10-N2	1.993	2.003
O11-H10	0.974	0.975	O11-H10	0.975	0.975
H12-O11	0.964	0.965	H12-O11	0.963	0.965
N3-N2-N1	122.27	122.09	C3-N2-N1	118.93	119.00
C4-N3-N2	119.44	119.31	N4-C3-N2	126.31	126.73
C5-C4-N3	121.86	121.92	C5-N4-C3	114.60	114.15
C6-N1-N2	119.44	119.25	C6-N1-N2	117.95	117.13
H7-C4-N3	115.48	115.31	H7-C3-N2	115.58	115.22
H8-C5-C4	122.43	122.28	H8-C5-N4	117.83	117.55
H9-C6-N1	115.42	115.23	H9-C6-N1	116.28	115.60
H10-N2-N1	120.92	125.16	H10-N2-N1	133.08	139.45
O11-H10-N2	145.81	146.83	O11-H10-N2	154.75	147.70
H12-O11-H10	104.48	103.52	H12-O11-H10	105.52	104.80
C4-N3-N2-N1	0.0	0.0	N4-C3-N2-N1	0.0	-0.4
C5-C4-N3-N2	-0.0	0.0	C5-N4-C3-N2	0.0	0.2
C6-N1-N2-N3	-0.0	-0.0	C6-N1-N2-C3	-0.0	0.2
H7-C4-N3-N2	180.0	180.0	H7-C3-N2-N1	180.0	179.5
H8-C5-C4-N3	180.0	180.0	H8-C5-N4-C3	-180.0	-179.9
H9-C6-N1-N2	-180.0	-180.0	H9-C6-N1-N2	180.0	-179.9
H10-N2-N1-C6	179.9	179.4	H10-N2-N1-C6	-179.7	173.8
O11-H10-N2-N1	-174.1	-168.5	O11-H10-N2-N1	179.8	-168.9
H12-O11-H10-N2	-6.6	-12.1	H12-O11-H10-N2	179.5	179.4

Table S11: Geometrical parameters of WII complexes of TZ135 and TZ1234 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TZ135-WII		Parameters	TTZ1234-WII	
	L1	L2		L1	L2
C2-N1	1.340	1.349	N2-N1	1.332	1.347
N3-C2	1.336	1.346	N3-N2	1.318	1.341
C4-N3	1.338	1.347	N4-N3	1.331	1.345
C5-C4	1.338	1.347	C5-N4	1.330	1.345
C6-N5	1.336	1.346	C6-N1	1.330	1.346
H7-C2	1.091	1.093	H7-C5	1.091	1.093
H8-C4	1.092	1.093	H8-C6	1.091	1.093
H9-C6	1.092	1.093	H9-N3	2.097	2.085
H10-N1	2.012	2.037	O10-H9	0.971	0.972
O11-H10	0.974	0.974	H11-O10	0.964	0.965
H12-O11	0.963	0.965	N3-N2-N1	121.53	121.51
N3-C2-N1	125.23	125.35	N4-N3-N2	122.36	122.48
C4-N3-C2	114.45	114.27	C5-N4-N3	117.85	117.30
C5-C4-N3	125.80	126.00	C6-N1-N2	118.13	117.66
C6-N5-C4	114.32	114.12	H7-C5-N4	116.85	116.34
H7-C2-N1	116.93	116.80	H8-C6-N1	116.86	116.35
H8-C4-N3	117.12	117.02	H9-N3-N2	116.41	112.60
H9-C6-N5	117.28	117.18	O10-H9-N3	140.41	139.86
H10-N1-C2	103.75	99.10	H11-O10-H9	104.55	103.66
O11-H10-N1	152.18	145.53	N4-N3-N2-N1	0.1	0.0
H12-O11-H10	105.76	104.97	C5-N4-N3-N2	-0.0	0.0
C4-N3-C2-N1	0.0	0.0	C6-N1-N2-N3	-0.1	-0.1
C5-C4-N3-C2	-0.0	-0.0	H7-C5-N4-N3	-180.0	180.0
C6-N5-C4-N3	0.0	-0.0	H8-C6-N1-N2	-180.0	-180.0
H7-C2-N1-C6	180.0	-180.0	H9-N3-N2-C1	179.7	179.7
H8-C4-N3-C2	180.0	-180.0	O10-H9-N3-N2	-16.3	-19.5
H9-C6-N5-C4	-180.0	-180.0	H11-O10-H9-N3	16.6	20.3
H10-N1-C2-N3	-180.0	179.6			
O11-H10-N1-C2	0.6	-0.5			
H12-O11-H10-N1	177.2	179.4			

Table S12: Geometrical parameters of WII complexes of TTZ1235 and TZ1245 at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TTZ1235-WII		Parameters	TTZ1245-WII	
	L1	L2		L1	L2
N2-N1	1.326	1.340	N2-N1	1.343	1.343
N3-N2	1.322	1.339	C3-N2	1.352	1.352
C4-N3	1.343	1.351	N4-C3	1.352	1.352
N5-C4	1.332	1.343	N5-N4	1.341	1.341
C6-N5	1.091	1.344	C6-N1	1.352	1.352
H7-C4	1.091	1.093	H7-C3	1.092	1.092
H8-C6	1.091	1.093	H8-C6	1.092	1.092
H9-N1	2.076	2.094	O9-H8	2.083	2.092
O10-H9	0.972	0.972	H10-N1	0.963	0.972
H11-O10	0.964	0.965	H11-O9	0.965	0.965
N3-N2-N1	120.25	119.61	C3-N2-N1	116.60	116.60
C4-N3-N2	117.95	118.18	N4-C3-N2	126.46	126.46
N5-C4-N3	125.51	125.68	N5-N4-C3	117.19	117.19
C6-N5-C4	112.90	112.74	C6-N1-N2	116.57	116.57
H7-C4-N3	116.06	116.07	H7-C3-N2	117.35	117.35
H8-C6-N5	119.25	119.18	H8-C6-N1	116.45	116.45
H9-N1-N2	139.16	141.55	O9-H8-C6	140.26	143.39
O10-H9-N1	140.76	135.86	H10-N1-N2	141.24	136.12
H11-O10-H9	105.84	105.02	H11-O9-H10	105.83	105.05
C4-N3-N2-N1	-0.0	-0.0	N4-C3-N2-N1	0.0	0.0
N5-C4-N3-N2	0.0	0.0	N5-N4-C3-N2	-0.0	-0.0
C6-N5-C4-N3	0.0	0.0	C6-N1-N2-C3	0.0	0.0
H7-C4-N3-N2	-180.0	-180.0	H7-C3-N2-N1	-180.0	-180.0
H8-C6-N5-C4	180.0	180.0	H8-C6-N1-N2	180.0	180.0
H9-N1-N2-N3	-180.0	-180.0	O9-H8-C6-N1	-179.4	179.2
O10-H9-N1-N2	180.0	180.0	H10-N1-N2-C3	179.2	-179.2
H11-O10-H9-N1	-180.0	180.0	H11-O9-H10-N1	-178.4	-179.9

Table S13: Geometrical parameters of PZ-WII and PY-WIII complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	PZ-WII		Parameters	PY-WIII	
	L1	L2		L1	L2
N2-N1	1.319	1.338	C2-N1	1.340	1.353
N3-N2	1.326	1.343	C3-C2	1.399	1.407
N4-N3	1.328	1.344	C4-C3	1.397	1.405
N5-N4	1.320	1.339	C5-C4	1.396	1.405
C6-N5	1.336	1.347	C6-N1	1.341	1.354
H7-C6	1.090	1.092	H7-C2	1.093	1.095
H8-N1	2.218	2.236	H8-C3	1.091	1.094
O9-H8	0.969	0.970	H9-C4	1.090	1.093
H10-O9	0.964	0.965	H10-C5	1.089	1.093
N3-N2-N1	120.21	119.67	H11-C6	1.093	1.095
N4-N3-N2	121.33	121.99	O12-H10	2.808	2.629
N5-N4-N3	120.52	119.99	H13-O12	0.965	0.966
C6-N5-N4	116.71	116.72	H14-O12	0.965	0.966
H7-C6-N5	118.63	118.44	C3-C2-N1	123.64	123.78
H8-N1-N2	143.76	144.74	C4-C3-C2	118.54	118.81
O9-H8-N1	127.38	123.51	C5-C4-C3	118.43	118.12
H10-O9-H8	105.92	105.06	C6-N1-C2	117.21	116.70
N4-N3-N2-N1	-0.4	-0.1	H7-C2-N1	116.10	115.84
N5-N4-N3-N2	0.2	0.1	H8-C3-C2	120.12	119.93
C6-N5-N4-N3	0.1	0.0	H9-C4-C3	121.52	121.82
H7-C6-N5-N4	179.6	179.9	H10-C5-C4	120.49	120.33
H8-N1-N2-N3	-178.3	179.8	H11-C6-N1	116.02	115.75
O9-H8-N1-N2	178.0	-179.9	O12-H10-C5	122.14	120.85
H10-O9-H8-N1	179.5	-180.0	H13-O12-H10	120.01	120.21
			H14-O12-H10	124.07	124.34
			C4-C3-C2-N1	0.0	-0.0
			C5-C4-C3-C2	0.0	0.0
			C6-N1-C2-C3	-0.0	-0.0
			H7-C2-N1-C3	-180.0	180.0
			H8-C3-C2-N1	-180.0	180.0
			H9-C4-C3-C2	-180.0	-180.0
			H10-C5-C4-C3	180.0	-180.0
			H11-C6-N1-C2	-180.0	-180.0
			O12-H10-C5-C4	-0.3	1.8
			H13-O12-H10-C5	112.8	108.3
			H14-O12-H10-C5	-108.9	-114.6

Table S14: Geometrical parameters of DZ12-WIII and DZ13-WIII complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	DZ12-WIII		Parameters	DZ13-WIII	
	L1	L2		L1	L2
N2-N1	1.334	1.351	C2-N1	1.339	1.350
C3-N2	1.339	1.353	N3-C2	1.339	1.350
C4-C3	1.400	1.407	C4-N3	1.341	1.352
C5-C4	1.386	1.397	C5-C4	1.395	1.402
C6-N1	1.339	1.353	C6-N1	1.341	1.352
H7-C3	1.092	1.094	H7-C2	1.092	1.094
H8-C4	1.089	1.092	H8-C4	1.093	1.095
H9-C5	1.089	1.092	H9-C5	1.089	1.091
H10-C6	1.092	1.094	H10-C6	1.092	1.094
O11-H9	2.715	2.593	O11-H9	2.613	2.510
H12-011	0.965	0.966	H12-O11	0.965	0.966
H13-011	0.965	0.966	H13-O11	0.965	0.966
C3-N2-N1	119.45	119.06	N3-C2-N1	127.15	127.47
C4-C3-N2	123.70	124.16	C4-N3-C2	115.88	115.62
C5-C4-C3	116.85	116.79	C5-C4-N3	122.30	122.21
C6-N1-N2	119.45	119.06	C6-N1-C2	115.90	115.62
H7-C3-N2	114.87	114.35	H7-C2-N1	116.44	116.28
H8-C4-C3	121.70	121.92	H8-C4-N3	116.49	116.35
H9-C5-C4	121.44	121.28	H9-C5-C4	122.58	122.66
H10-C6-N1	114.87	114.35	H10-C6-N1	117.12	117.10
O11-H9-C5	121.43	119.54	O11-H9-C5	128.19	117.68
H12-011-H9	123.33	123.08	H12-O11-H9	127.48	128.06
H13-011-H9	122.29	121.99	H13-O11-H9	124.33	124.39
C4-C3-N2-N1	-0.0	-0.0	C4-N3-C2-N1	-0.0	-0.0
C5-C4-C3-N2	-0.0	0.0	C5-C4-N3-C2	0.0	0.0
C6-N1-N2-C3	0.0	0.0	C6-N1-C2-N3	-0.0	0.0
H7-C3-N2-N1	180.0	180.0	H7-C2-N1-C6	180.0	180.0
H8-C4-C3-N2	180.0	-180.0	H8-C4-N3-C2	-180.0	-180.0
H9-C5-C4-C3	-180.0	-180.0	H9-C5-C4-N3	-180.0	180.0
H10-C6-N1-N2	-180.0	180.0	H10-C6-N1-C2	-180.0	-180.0
O11-H9-C5-C4	0.1	0.2	O11-H9-C5-C4	-179.0	-177.7
H12-011-H9-C5	109.0	110.6	H12-O11-H9-C5	-103.3	-105.7
H13-011-H9-C5	-110.1	-111.4	H13-O11-H9-C5	100.8	99.5

Table S15: Geometrical parameters of DZ14-WIII and TZ123-WIII complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	DZ14-WIII		Parameters	TZ123-WIII	
	L1	L2		L1	L2
C2-N1	1.339	1.347	N2-N1	1.326	1.345
C3-C2	1.401	1.399	N3-N2	1.327	1.346
N4-C3	1.339	1.347	C4-N3	1.342	1.353
C5-N4	1.339	1.347	C5-C4	1.389	1.398
C6-N1	1.339	1.347	C6-N1	1.343	1.353
H7-C2	1.091	1.086	H7-C4	1.090	1.092
H8-C3	1.091	1.086	H8-C5	1.089	1.091
H9-C5	1.093	1.088	H9-C6	1.091	1.094
H10-C6	1.093	1.088	O10-H8	2.560	2.491
O11-H8	2.734	2.597	H11-O10	0.965	0.966
H12-O11	0.965	0.972	H12-O10	0.965	0.966
H13-O11	0.965	0.972	N3-N2-N1	121.58	121.32
C3-C2-N1	122.01	122.30	C4-N3-N2	119.74	119.67
N4-C3-C2	122.01	122.30	C5-C4-N3	122.03	122.08
C5-N4-N3	115.94	115.33	C6-N1-N2	119.75	119.63
C6-N1-C2	115.94	115.33	H7-C4-N3	116.08	116.04
H7-C2-N1	117.84	117.54	H8-C5-C4	121.62	121.40
H8-C3-C2	120.16	121.10	H9-C6-N1	115.35	115.17
H9-C5-N4	117.23	116.66	O10-H8-C5	125.95	122.02
H10-C6-N1	117.23	116.66	H11-O10-H8	126.17	126.59
O11-H8-C3	122.77	121.10	H12-O10-H8	125.79	124.77
H12-O11-H8	122.75	121.73	C4-N3-N2-N1	-0.0	-0.0
H13-O11-H8	123.07	122.27	C5-C4-N3-N2	0.0	0.0
N4-C3-C2-N1	0.0	0.0	C6-N1-N2-N3	0.0	0.0
C5-N4-N3-C2	0.0	-0.0	H7-C4-N3-N2	-180.0	-180.0
C6-N1-C2-C3	-0.0	-0.0	H8-C5-C4-N3	-180.0	-180.0
H7-C2-N1-C6	180.0	-180.0	H9-C6-N1-N2	-180.0	180.0
H8-C3-C2-N1	-180.0	-180.0	O10-H8-C5-C6	-179.9	-179.5
H9-C5-N4-C3	180.0	-180.0	H11-O10-H8-C5	-102.0	-104.9
H10-C6-N1-C2	-180.0	180.0	H12-O10-H8-C5	101.7	103.9
O11-H8-C3-C2	0.1	0.6			
H12-O11-H8-C3	109.3	109.6			
H13-O11-H8-C3	-109.4	-111.4			

Table S16: Geometrical parameters of TZ124-WIII and TTZ1234-WIII complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TZ124-WIII		Parameters	TTZ1234-WIII	
	L1	L2		L1	L2
N2-N1	1.335	1.350	N2-N1	1.337	1.349
C3-N2	1.337	1.349	N3-N2	1.317	1.342
N4-C3	1.342	1.353	N4-N3	1.337	1.349
C5-N4	1.330	1.345	C5-N4	1.329	1.346
C6-N1	1.334	1.350	C6-N1	1.329	1.346
H7-C3	1.091	1.093	H7-C5	1.090	1.092
H8-C5	1.091	1.093	H8-C6	1.090	1.092
H9-C6	1.090	1.092	O9-H8	2.638	2.536
O10-H9	2.709	2.561	H10-O9	0.965	0.967
H11-O10	0.965	0.966	H11-H10	0.965	0.967
H12-O10	0.965	0.966	N3-N2-N1	121.81	121.85
C3-N2-N1	118.17	118.12	N4-N3-N2	121.86	121.85
N4-C3-N2	127.01	127.52	C5-N4-N3	118.10	117.67
C5-N4-C3	114.43	113.97	C6-N1-N2	118.11	117.67
C6-N1-N2	118.25	117.53	H7-C5-N4	117.74	117.28
H7-C3-N2	115.52	115.20	H8-C6-N1	117.76	117.29
H8-C5-N4	118.62	118.36	O9-H8-C6	119.00	117.43
H9-C6-N1	116.98	116.41	H10-O9-H8	121.89	121.95
O10-H9-C6	119.50	119.44	H11-H10-O9	122.14	122.23
H11-O10-H9	121.24	121.14	N4-N3-N2-N1	0.0	0.0
H12-O10-H9	121.47	122.32	C5-N4-N3-N2	-0.0	-0.0
N4-C3-N2-N1	0.0	-0.0	C6-N1-N2-N3	-0.0	-0.0
C5-N4-C3-N2	-0.0	0.0	H7-C5-N4-N3	180.0	-180.0
C6-N1-N2-C3	0.0	0.0	H8-C6-N1-N2	180.0	-180.0
H7-C3-N2-N1	-180.0	180.0	O9-H8-C6-N1	180.0	-179.8
H8-C5-N4-C3	180.0	180.0	H10-O9-H8-C6	-111.1	-112.2
H9-C6-N1-N2	180.0	180.0	H11-O9-H8-C6	110.8	111.3
O10-H9-C6-N1	179.9	-179.8			
H11-O10-H9-C6	-112.0	-112.8			
H12-O10-H9-C6	111.9	111.8			

Table S17: Geometrical parameters of PY-WIV and DZ12-WIV complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	PY-WIV		Parameters	DZ12-WIV	
	L1	L2		L1	L2
C2-N1	1.341	1.348	N2-N1	1.345	1.349
C3-C2	1.398	1.397	C3-N2	1.350	1.358
C4-C3	1.397	1.397	C4-C3	1.401	1.408
C5-C4	1.397	1.397	C5-C4	1.386	1.397
C6-N1	1.341	1.348	C6-N1	1.341	1.356
H7-C2	1.089	1.089	H7-C3	1.093	1.098
H8-C3	1.087	1.088	H8-C4	1.089	1.094
H9-C4	1.087	1.087	H9-C5	1.089	1.094
H1O-C5	1.087	1.088	H10-C6	1.092	1.094
H11-C6	1.089	1.089	O11-H9	2.221	2.227
O12-H9	2.325	2.256	H12-O11	0.961	0.966
H13-O12	0.969	0.972	H13-O11	0.961	0.966
H14-O12	0.970	0.972	C3-N2-N1	119.45	119.06
C3-C2-N1	123.69	123.73	C4-C3-N2	123.70	124.16
C4-C3-C2	118.74	118.99	C5-C4-C3	115.85	114.79
C5-C4-C3	118.07	117.92	C6-N1-N2	119.45	119.06
C6-N1-C2	117.08	116.66	H7-C3-N2	114.87	114.35
H7-C2-N1	115.86	115.58	H8-C4-C3	121.70	122.92
H8-C3-C2	120.18	120.06	H9-C5-C4	121.44	121.28
H9-C4-C3	120.98	120.99	H10-C6-N1	115.87	114.53
H1O-C5-C4	121.08	120.95	O11-H9-C5	179.08	179.28
H11-C6-N1	115.86	115.59	H12-O11-H9	125.33	125.08
O12-H9-C4	176.28	178.91	H13-O11-H9	124.29	124.99
H13-O12-H9	129.98	126.50	C4-C3-N2-N1	-0.0	-0.0
H14-O12-H9	124.48	125.20	C5-C4-C3-N2	-0.0	0.0
C4-C3-C2-N1	-0.0	0.1	C6-N1-N2-C3	0.0	0.0
C5-C4-C3-C2	0.1	-0.1	H7-C3-N2-N1	180.0	180.0
C6-N1-C2-C3	-0.0	-0.1	H8-C4-C3-N2	180.0	-180.0
H7-C2-N1-C3	-180.1	-180.0	H9-C5-C4-C3	-180.0	-180.0
H8-C3-C2-N1	-179.9	-179.9	H10-C6-N1-N2	-180.0	180.0
H9-C4-C3-C2	-179.8	180.0	O11-H9-C5-C4	120.1	121.5
H1O-C5-C4-C3	180.0	-180.0	H12-O11-H9-C5	-38.1	-37.6
H11-C6-N1-C2	-180.0	180.0	H13-O11-H12-H9	139.1	140.4
O12-H9-C4-C3	96.5	-79.2			
H13-O12-H9-C4	170.8	168.2			
H14-O12-H9-C4	-6.0	-9.7			

Table S18: Geometrical parameters of DZ13-WIV and DZ14-WIII complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	DZ13-WIV		Parameters	DZ14-WIV	
	L1	L2		L1	L2
C2-N1	1.338	1.344	C2-N1	1.339	1.346
N3-C2	1.338	1.344	C3-C2	1.398	1.397
C4-N3	1.341	1.347	N4-C3	1.339	1.346
C5-C4	1.395	1.394	C5-N4	1.341	1.349
C6-N1	1.341	1.347	C6-N1	1.339	1.346
H7-C2	1.088	1.087	H7-C2	1.088	1.088
H8-C4	1.089	1.088	H8-C3	1.088	1.088
H9-C5	1.086	1.086	H9-C5	1.088	1.087
H10-C6	1.089	1.088	H10-C6	1.088	1.088
O11-H9	2.288	2.232	O11-H9	2.308	2.248
H12-O11	0.970	0.972	H12-O11	0.969	0.972
H13-O11	0.970	0.972	H13-O11	0.969	0.972
N3-C2-N1	127.10	127.22	C3-C2-N1	122.00	122.29
C4-N3-C2	115.83	115.60	N4-C3-C2	122.12	122.40
C5-C4-N3	122.57	122.56	C5-N4-N3	116.07	115.53
C6-N1-C2	115.83	115.60	C6-N1-C2	115.84	115.24
H7-C2-N1	116.45	116.39	H7-C2-N1	117.04	116.66
H8-C4-N3	116.29	116.09	H8-C3-C2	120.85	120.94
H9-C5-C4	122.0	121.78	H9-C5-N4	117.35	117.25
H10-C6-N1	116.30	116.10	H10-C6-N1	116.98	116.63
O11-H9-C5	178.29	179.63	O11-H9-C5	178.99	178.34
H12-O11-H9	126.80	127.10	H12-O11-H9	114.15	120.52
H13-O11-H9	127.67	127.63	H13-O11-H9	112.13	120.32
C4-N3-C2-N1	-0.0	0.0	N4-C3-C2-N1	0.0	-0.0
C5-C4-N3-C2	-0.0	-0.0	C5-N4-C3-C2	0.0	0.0
C6-N1-C2-N3	0.0	-0.0	C6-N1-C2-C3	-0.0	0.0
H7-C2-N1-C6	-180.0	180.0	H7-C2-N1-C6	180.0	-180.0
H8-C4-N3-C2	-180.0	180.0	H8-C3-C2-N1	-180.0	-180.0
H9-C5-C4-N3	-180.0	-180.0	H9-C5-N4-C3	180.0	180.0
H10-C6-N1-C2	180.0	-180.0	H10-C6-N1-C2	-180.0	-180.0
O11-H9-C5-C4	119.5	121.6	O11-H9-C5-N4	-174.0	-178.4
H12-O11-H9-C5	-28.7	-31.6	H12-O11-H9-C5	-121.9	-114.6
H13-O11-H9-C5	149.1	148.3	H13-O11-H9-C5	118.3	111.1

Table S19: Geometrical parameters of TZ123-WIII and TZ124-WIV complexes at wB97XD/aug-cc-pVDZ (L1) and MP2/aug-cc-pVDZ (L2). Distances are in Å and angles are in degrees.

Parameters	TZ123-WIV		Parameters	TZ124-WIV	
	L1	L2		L1	L2
N2-N1	1.327	1.343	N2-N1	1.336	1.349
N3-N2	1.327	1.342	C3-N2	1.336	1.343
C4-N3	1.342	1.348	N4-C3	1.342	1.348
C5-C4	1.389	1.390	C5-N4	1.332	1.341
C6-N1	1.342	1.348	C6-N1	1.333	1.343
H7-C4	1.087	1.087	H7-C3	1.087	1.086
H8-C5	1.087	1.087	H8-C5	1.089	1.088
H9-C6	1.087	1.087	H9-C6	1.087	1.087
O10-H8	2.226	2.186	O10-H8	2.242	2.203
H11-O10	0.970	0.973	H11-O10	0.969	0.972
H12-O10	0.970	0.973	H12-O10	0.969	0.972
N3-N2-N1	121.39	121.02	C3-N2-N1	118.04	117.95
C4-N3-N2	119.75	119.58	N4-C3-N2	127.13	127.44
C5-C4-N3	122.37	122.55	C5-N4-C3	114.57	114.32
C6-N1-N2	119.74	119.57	C6-N1-N2	118.19	117.52
H7-C4-N3	115.21	114.95	H7-C3-N2	115.51	115.34
H8-C5-C4	122.83	122.64	H8-C5-N4	118.14	117.83
H9-C6-N1	115.21	114.96	H9-C6-N1	116.14	115.48
O10-H8-C5	178.65	179.41	O10-H8-C5	177.70	179.48
H11-O10-H8	126.99	127.20	H11-O10-H8	118.26	121.18
H12-O10-H8	127.53	127.56	H12-O10-H8	120.46	122.38
C4-N3-N2-N1	0.0	0.0	N4-C3-N2-N1	0.0	0.0
C5-C4-N3-N2	-0.0	-0.0	C5-N4-C3-N2	-0.0	0.0
C6-N1-N2-N3	-0.0	-0.0	C6-N1-N2-C3	-0.0	-0.0
H7-C4-N3-N2	180.0	-180.0	H7-C3-N2-N1	-180.0	-180.0
H8-C5-C4-N3	180.0	-180.0	H8-C5-N4-C3	-180.0	-180.0
H9-C6-N1-N2	-180.0	180.0	H9-C6-N1-N2	180.0	180.0
O10-H8-C5-C4	-102.4	-102.1	O10-H8-C5-C6	-56.9	-88.8
H11-O10-H8-C5	12.6	11.5	H11-O10-H8-C5	-62.6	-23.9
H12-O10-H8-C5	-167.7	-167.8	H12-O10-H8-C5	165.6	-162.3

S4. REFERENCES

[1] Carroll, M. T.; Chang, C.; Bader, R. F. W. Prediction of the structures of hydrogen-bonded complexes using the laplacian of the charge density. *Mol. Phys.* **1988**, *63*, 387-405.

[2] Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. Bonded and nonbonded charge concentrations and their relation to molecular geometry and reactivity. *J. Am. Chem. Soc*. **1984**, *106*, 1594-1605**.**

[3] Bader, R. F. W.; Heard, G. L. The mapping of the conditional pair density onto the electron density. *J. Chem. Phys*. **1999,** *111***,** 8789-8798**.**