Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Competition between $n \rightarrow \pi^*_{Ar}$ and conventional hydrogen bonding (N-H...N) interactions: An ab initio study of the complexes of 7-azaindole and fluorosubstituted pyridines

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Table S1 Geometrical parameters of the complexes of 7-AI with 2,6-FP, 2,3,6-FP, 2,4,6-FP, 2,3,4,6-FP, 2,3,5,6-FP and 2,3,4,5,6-FP calculated at various DFT (B3LYP, M05-2X, B97-D) as well as MP2 levels of theory using aug-cc-pVDZ (aVDZ) and cc-pVTZ basis sets

		7-AI…2,6-FP	7AI…2,4,6-FP	7AI…2,3,6-FP	7AI…2,3,4,6-FP	7AI…2,3,5,6-FP	7AI…2,3,4,5,6-FP
B3LYP/aVDZ	$d_{(N\text{-}H\ldots N)}$ (Å)	2.13	2.17	2.19	2.24	2.27	2.31
	$R_{(N\ldots Ar)}$ (Å)	4.68	4.05	3.99	3.62	3.58	3.40
	$\theta_{\angle\ N\text{-}H\ldots N}$ (deg)	168	156	154	148	147	145
M05-2X/aVDZ	$d_{(N\text{-}H\ldots N)}$ (Å)	2.21	2.25	2.26	2.28	2.30	2.33
	$R_{(N\ldots Ar)}$ (Å)	3.15	3.08	3.08	3.01	3.01	2.97
	$\theta_{\angle\ N\text{-}H\ldots N}$ (deg)	142	141	140	139	139	138
B97-D/aVDZ	$d_{(N\text{-}H\ldots N)}$ (Å)	2.14	2.18	2.20	2.26	2.28	2.30
	$R_{(N\ldots Ar)}$ (Å)	3.20	3.09	3.09	3.00	2.99	2.96
	$\theta_{\angle\ N\text{-}H\ldots N}$ (deg)	144	143	142	141	140	140
MP2/aVDZ	$d_{(N\text{-}H\ldots N)}$ (Å)	2.11	2.14	2.15	2.18	2.18	2.21
	$R_{(N\ldots Ar)}$ (Å)	2.88	2.84	2.82	2.80	2.78	2.76
	$\theta_{\angle\ N\text{-}H\ldots N}$ (deg)	139	139	138	138	137	137
M05-2X/cc-pVTZ	$d_{(N\text{-}H\ldots N)}$ (Å)	2.20	2.24	2.25	2.28	2.29	2.34
	$R_{(N\ldots Ar)}$ (Å)	3.22	3.13	3.13	3.05	3.07	2.97
	$\theta_{\angle\ N\text{-}H\ldots N}$ (deg)	143	141	141	140	140	139

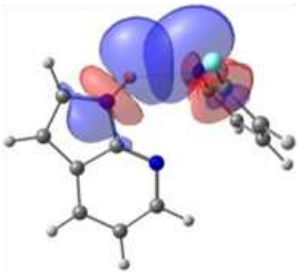
Table S2 Different components of the total interaction energy (kcal/mol) of the complexes of 7-AI with 2,6-substituted fluoropyridines calculated at the M05-2X/cc-pVDZ level of theory using LMO-EDA method

	ΔE_{elec}	ΔE_{ex}	ΔE_{rep}	ΔE_{pol}	ΔE_{dis}	ΔE_{tot}
7-AI···2,6-FP	-9.46	-6.59	22.65	-3.13	-8.5	-5.03
7-AI···2,4,6-FP	-9.92	-7.26	24.85	-2.84	-10.14	-5.31
7-AI···2,3,6-FP	-9.55	-7.02	24.27	-2.81	-10.03	-5.14
7-AI···2,3,4,6-FP	-10.39	-7.66	26.08	-2.74	-10.77	-5.48
7-AI···2,3,5,6-FP	-10.02	-7.42	25.47	-2.76	-10.61	-5.34
7-AI···2,3,4,5,6-FP	-10.78	-7.9	26.73	-2.65	-11.15	-5.74

Table S3 Different components of the total interaction energy (kcal/mol) of the double hydrogen bonded complexes of 7-AI with 2,3-FP, 2,3,4-FP and 2,3,4,5-FP calculated at the M05-2X/cc-pVDZ level of theory using LMO-EDA method

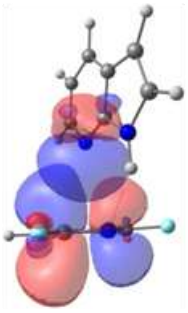
	ΔE_{elec}	ΔE_{ex}	ΔE_{rep}	ΔE_{pol}	ΔE_{dis}	ΔE_{tot}
7-AI···2,3-FP	-12.26	-7.16	22.18	-4.10	-6.66	-8.0
7-AI···2,3,4-FP	-12.40	-7.20	22.36	-4.10	-6.73	-8.06
7-AI···2,3,4,5-FP	-12.21	-7.10	22.17	-3.96	-6.78	-7.88

7-AI…2,6-FP



$n_{N(FP)} \rightarrow \sigma^*_{NH(7-AI)}$

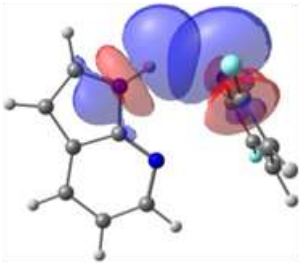
$E^{(2)}_{i \rightarrow j^*} = 6.58$ kcal/mol



$n_{N(7-AI)} \rightarrow \pi^*_{C-N(FP)}$

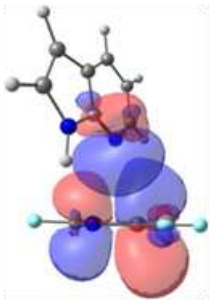
$E^{(2)}_{i \rightarrow j^*} = 0.41$ kcal/mol

7-AI…2,3,6-FP



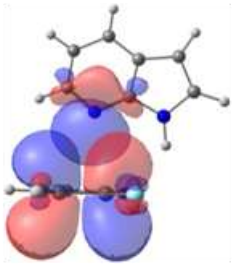
$n_{N(FP)} \rightarrow \sigma^*_{NH(7-AI)}$

$E^{(2)}_{i \rightarrow j^*} = 5.65$ kcal/mol



$n_{N(7-AI)} \rightarrow \pi^*_{C-N(FP)}$

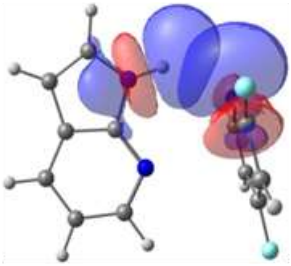
$E^{(2)}_{i \rightarrow j^*} = 0.49$ kcal/mol



$n_{N(7-AI)} \rightarrow \pi^*_{C-C(FP)}$

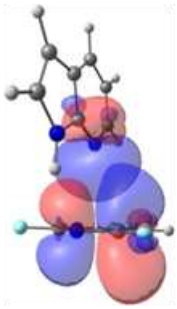
$E^{(2)}_{i \rightarrow j^*} = 0.10$ kcal/mol

7-AI…2,4,6-FP



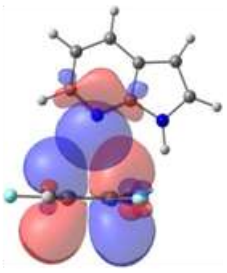
$n_{N(FP)} \rightarrow \sigma^*_{NH(7-AI)}$

$E^{(2)}_{i \rightarrow j^*} = 5.75$ kcal/mol



$n_{N(7-AI)} \rightarrow \pi^*_{C-N(FP)}$

$E^{(2)}_{i \rightarrow j^*} = 0.46$ kcal/mol



$n_{N(7-AI)} \rightarrow \pi^*_{C-C(FP)}$

$E^{(2)}_{i \rightarrow j^*} = 0.18$ kcal/mol

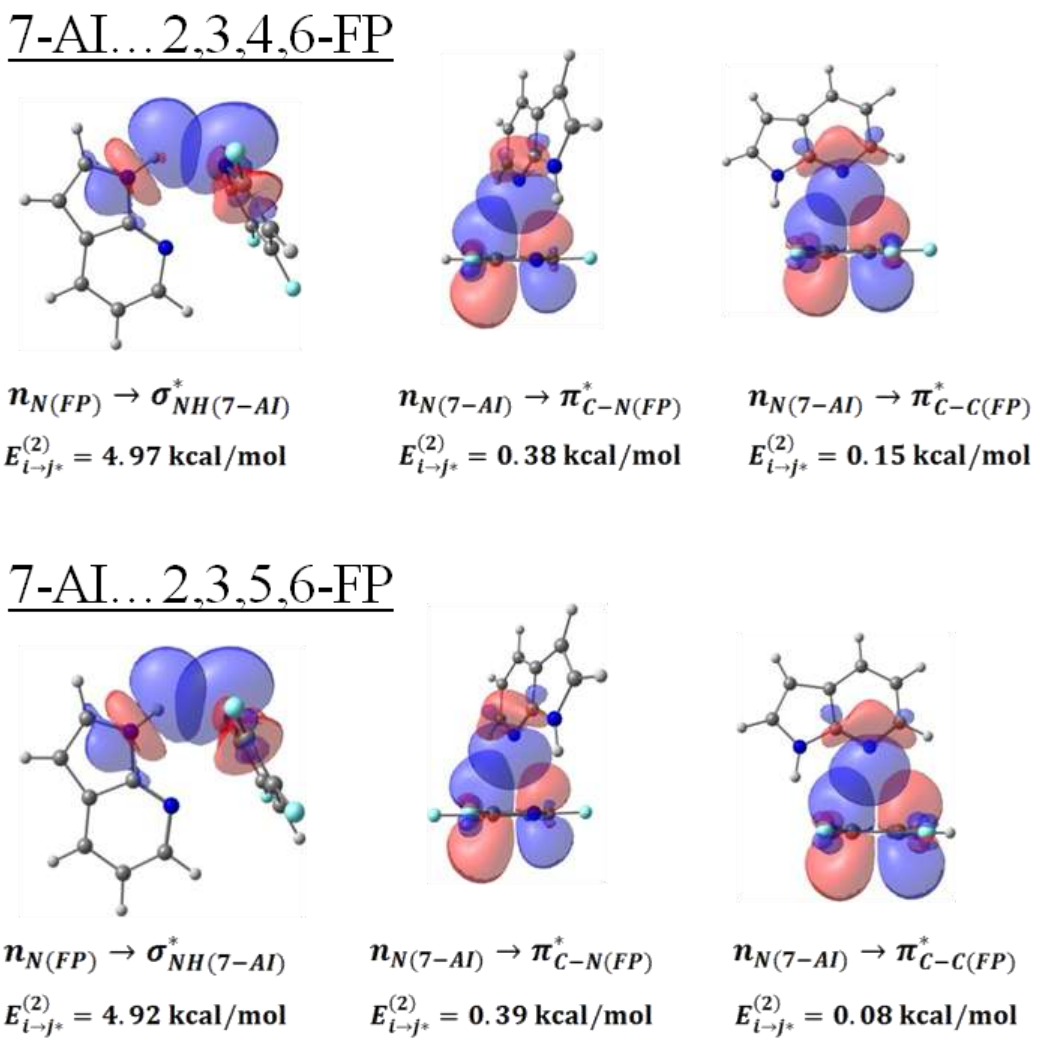


Figure S1. The NBO pictures depicting the overlap between the donor and acceptor orbitals corresponding to the n$\rightarrow\pi^*_{Ar}$ and N-H...N interactions present in the complexes of 7-AI with 2,6-FP, 2,3,6-FP, 2,4,6-FP, 2,3,4,6-FP, and 2,3,5,6-FP .