

Supplementary Information

Table SI. Main geometrical parameters (bond lengths and angles in angstroms and degrees, respectively) for complexes $n^-\cdot\text{HF}$ and $n\cdot X^-$ ($n = 1-5$, $X = \text{Cl}$, Br , AcO , and H_2PO_4) at the B3LYP/6-31G(d,p) level.

n	$n^-\cdot\text{HF}$			$n\cdot\text{Cl}^-$			$n\cdot\text{Br}^-$		
	$R_{\text{N}\cdots\text{H}}$	$R_{\text{H}\cdots\text{F}}$	$\theta_{\text{N}\cdots\text{H}\cdots\text{F}}$	$R_{\text{N}\cdots\text{H}}$	$R_{\text{H}\cdots\text{Cl}}$	$\theta_{\text{N}\cdots\text{H}\cdots\text{Cl}}$	$R_{\text{N}\cdots\text{H}}$	$R_{\text{H}\cdots\text{Br}}$	$\theta_{\text{N}\cdots\text{H}\cdots\text{Br}}$
1	1.474	1.027	174.5	1.053	2.055	170.2	1.041	2.302	167.9
2	1.479	1.024	175.5	1.054	2.050	170.0	1.041	2.311	167.4
3	1.490	1.019	176.0	1.055	2.042	168.6	1.039	2.235	174.5
4	1.489	1.015	176.0	1.055	2.049	167.4	1.040	2.231	176.0
5	1.489	1.020	174.6	1.058	2.019	171.0	1.046	2.256	169.1

n	$n\cdot\text{AcO}^-$			$n\cdot\text{H}_2\text{PO}_4^-$		
	$R_{\text{N}\cdots\text{H}}$	$R_{\text{H}\cdots\text{O}}$	$\theta_{\text{N}\cdots\text{H}\cdots\text{O}}$	$R_{\text{N}\cdots\text{H}}$	$R_{\text{H}\cdots\text{O}}$	$\theta_{\text{N}\cdots\text{H}\cdots\text{O}}$
1	1.077	1.582	172.1	1.061	1.613	171.6
2	1.080	1.567	172.6	1.062	1.601	172.8
3	1.090	1.534	171.6	1.046	1.720	170.4
4	1.089	1.555	169.7	1.070	1.570	172.6
5	1.084	1.555	172.8	1.042	1.699	172.9

Table SII. Main geometrical parameters (bond lengths and angles in angstroms and degrees, respectively) and the interaction energies of complexes $\text{AIC}^-\cdot\text{HF}$ and $\text{AIC}\cdot X^-$ ($X = \text{Cl}$ and Br) at the MP2/6-31+G(d,p) level.

Complexes	$R_{\text{H7}\cdots\text{N1}}$	$R_{\text{H7}\cdots\text{X}}$	$\theta_{\text{N1}\cdots\text{H7}\cdots\text{X}}$	ΔE
AIC	1.022			
$\text{AIC}^-\cdot\text{HF}$	1.468	1.026	174.8	-37.2
$\text{AIC}\cdot\text{Cl}^-$	1.040	2.138	165.4	-18.1
$\text{AIC}\cdot\text{Br}^-$	1.035	2.254	171.4	-27.3

Table SIII. Electronic density at BCP $\rho(r)_{\text{bcp}}$, the Laplacian $\nabla^2\rho(r)_{\text{bcp}}$ (all in au), and the bond energy E_{HB} (in kcal/mol) of complexes $n\cdot\text{HF}^-$ and $n\cdot X^-$ ($n = 1-5$, $X = \text{Cl}$, Br , AcO , and H_2PO_4) at the B3LYP/6-31G(d,p) level.

n	$n^-\cdot\text{HF}$						$n\cdot\text{Cl}^-$					
	$\text{H}\cdots\text{N}$			$\text{H}\cdots\text{F}$			$\text{H}\cdots\text{N}$			$\text{H}\cdots\text{Cl}$		
	$\rho(r)_{\text{bcp}}$	$\nabla^2\rho(r)_{\text{bcp}}$	E_{HB}	$\rho(r)_{\text{bcp}}$	$\nabla^2\rho(r)_{\text{bcp}}$	E_{HB}	$\rho(r)_{\text{bcp}}$	$\nabla^2\rho(r)_{\text{bcp}}$	E_{HB}	$\rho(r)_{\text{bcp}}$	$\nabla^2\rho(r)_{\text{bcp}}$	E_{HB}
1	0.0918	0.0472	-29.3	0.2529	-1.055	-148.4	0.3002	-1.5895	-152.8	0.0361	0.0655	-7.4
2	0.0905	0.0529	-28.7	0.2554	-1.0875	-150.9	0.2994	-1.5825	-152.5	0.0365	0.0659	-7.5
3	0.0876	0.0633	-27.2	0.2698	-1.1458	-155.1	0.2977	-1.5692	-151.6	0.0373	0.0663	-7.6
4	0.0855	0.0703	-26.2	0.2628	-1.1893	-158.2	0.2980	-1.5725	-151.7	0.0367	0.0656	-7.5
5	0.0889	0.0594	-27.9	0.2587	-1.1280	-154.1	0.2960	-1.5560	-150.7	0.0391	0.0678	-8.1

Table SIII. Cont.

<i>n</i>	<i>n</i> [−] ·Br [−]						<i>n</i> ·H ₂ PO ₄ [−]					
	H–N			H...Br			H–N			H...H ₂ PO ₄		
	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}
1	0.3108	−1.6676	−158.2	no*	no	no	0.2927	−1.5396	−149.1	0.0545	0.1507	−13.6
2	0.3111	−1.6688	−158.4	0.0255	0.0474	−4.4	0.2908	−1.5227	−148.2	0.0562	0.1532	−14.3
3	0.3125	−1.6603	−159.9	0.0301	0.0536	−5.5	0.3060	−1.6466	−155.8	0.0409	0.1222	−9.4
4	0.3116	−1.6542	−159.4	0.0304	0.0537	−5.6	0.2840	−1.4675	−144.7	0.0613	0.1576	−16.2
5	0.3072	−1.6392	−156.3	0.0286	0.0504	−5.1	0.3097	−1.6682	−158.0	0.0422	0.1321	−9.9

<i>n</i>	<i>n</i> [−] ·AcO [−]					
	H–N			H...AcO		
	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}	$\rho(r)_{bcp}$	$\nabla^2\rho(r)_{bcp}$	E_{HB}
1	0.2794	−1.4316	−142.0	0.0622	0.1455	−15.9
2	0.2764	−1.4055	−140.5	0.0647	0.1466	−16.9
3	0.2685	−1.3389	−136.4	0.0710	0.1462	−19.5
4	0.2637	−1.2993	−133.9	0.0747	0.1441	−21.2
5	0.2737	−1.3845	−139.1	0.0669	0.1471	−17.8

Table SIV. The NBO charges of complexes AIC[−]·HF and AIC·X[−] (X = Cl, Br, AcO, and H₂PO₄).

Complexes	X [−]	AIC	AIC [−]	HX
AIC [−] ·HF			−0.8564	−0.1436
AIC·Cl [−]	−0.9015	−0.0981		
AIC·Br [−]	−0.9280	−0.0717		
AIC·AcO [−]	−0.8801	−0.1199		
AIC·H ₂ PO ₄ [−]	−0.9334	−0.0596		

Figure SI. FMOs of AIC and AIC[−] in S₁ at the TD-CAM-B3LYP/6-31+G(d,p) level.