Effect of the H-bonding and complexation with metal ions on π-electron structure of adenine tautomers

Olga A. Stasyuk,[a] Halina Szatyłowicz,*[a] Tadeusz M. Krygowski[b]*

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw (Poland) *ostasyuk@ch.pw.edu.pl* *halina@ch.pw.edu.pl*
[b] Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw (Poland) *tmkryg@chem.uw.edu.pl*

Supplementary Information

Table S1 Comparison of HOMA and HOMED indices for adenine tautomers, and angle of pyramidality of the NH_2 group

Tautomer	E_{rel}/ kcal/mol	HOMA5	HOMA6	$HOMA_{tot}$	HOMED5	HOMED6	$HOMED_{tot}$	Angle φ /°
1H adenine	17.96	0.857	0.797	0.862	0.947	0.870	0.907	14.2
3H adenine	7.80	0.923	0.920	0.928	0.953	0.942	0.942	0.0
7H adenine	7.68	0.857	0.982	0.923	0.884	0.994	0.932	15.6
9H adenine	0.00	0.869	0.984	0.926	0.887	0.997	0.935	3.9

Table S2 Relative energies and HOMA values for tautomers of purine and 6-nitropurine

	Purine				**6-nitropurine**			
Tautomer	E_{rel}/ kcal/mol	HOMA5	HOMA6	$HOMA_{tot}$	E_{rel}/ kcal/mol	HOMA5	HOMA6	$HOMA_{tot}$
1H	13.09	0.67	0.67	0.78	16.18	0.78	0.82	0.86
3H	9.88	0.77	0.82	0.85	14.04	0.50	0.55	0.72
7H	3.97	0.83	0.97	0.91	0.00	0.84	0.94	0.91
9H	0.00	0.83	0.98	0.92	3.02	0.85	0.97	0.92

Table S3 Differences between HOMA values for H-bonded complexes and free adenine tautomers

Active center	E_{HB} / kcal/mol	$d_{N\cdots H}$ / Å	HOMA6	HOMA5	HOMAtot	ΔHOMA6	ΔHOMA5	$\Delta HOMA_{tot}$
1-H adenine			**0.797**	**0.857**	**0.862**			
N1-···HF	-22.21	1.447	0.926	0.902	0.935	0.129	0.045	0.073
N3···HF	-10.41	1.707	0.816	0.863	0.873	0.019	0.006	0.011
N7···HF	-18.74	1.478	0.844	0.923	0.894	0.047	0.066	0.032
N9···HF	-13.59	1.648	0.833	0.888	0.883	0.036	0.031	0.021
N10···HF	-6.48	1.728	0.751	0.781	0.833	-0.046	-0.076	-0.029
H14···F-	-25.06	1.383	0.800	0.931	0.864	0.003	0.074	0.002
H15···F-	-22.00	1.547	0.725	0.915	0.820	-0.072	0.058	-0.042
3-H adenine			**0.920**	**0.923**	**0.928**			
N1···HF	-11.10	1.624	0.913	0.923	0.924	-0.007	0.003	0.001
N3-···HF	-21.49	1.540	0.947	0.908	0.947	0.027	-0.015	0.019
N7···HF	-17.72	1.518	0.923	0.953	0.935	0.003	0.030	0.007
N9···HF	-15.55	1.594	0.945	0.937	0.940	0.025	0.014	0.012
N10···HF	-4.64	1.819	0.910	0.890	0.919	-0.010	-0.033	-0.009
H14···F-	-25.13	1.485	0.748	0.948	0.824	-0.172	0.025	-0.104
H15···F-	-23.76	1.517	0.725	0.941	0.809	-0.195	0.018	-0.119
7-H adenine			**0.982**	**0.857**	**0.923**			
N1···HF	-13.17	1.588	0.976	0.870	0.926	-0.006	0.013	0.003
N3···HF	-11.77	1.676	0.985	0.874	0.933	0.003	0.017	0.010
N7-···HF	-25.59	1.358	0.965	0.924	0.951	-0.017	0.067	0.028
N9···HF	-11.35	1.689	0.984	0.870	0.930	0.002	0.013	0.007
N10···HF	-9.05	1.656	0.971	0.868	0.930	-0.011	0.011	0.007
H14···F-	-25.99	1.467	0.902	0.858	0.870	-0.080	0.001	-0.053
H15···F-	-25.59	1.070	0.965	0.924	0.951	-0.017	0.067	0.028
9-H adenine			**0.984**	**0.869**	**0.926**			
N1···HF	-13.49	1.589	0.978	0.878	0.926	-0.006	0.009	0.000
N3···HF	-13.49	1.624	0.982	0.886	0.933	-0.002	0.017	0.007
N7···HF	-14.04	1.588	0.973	0.877	0.922	-0.011	0.008	-0.004
N9-···HF	-23.69	1.506	0.960	0.909	0.947	-0.024	0.040	0.021
N10···HF	-5.87	1.789	0.990	0.868	0.931	0.006	-0.001	0.005
H14···F-	-26.39	1.459	0.838	0.851	0.828	-0.146	-0.018	-0.098
H15···F-	-26.16	1.472	0.833	0.849	0.825	-0.151	-0.020	-0.101

* In Table S3 the changes of HOMA values are presented as differences between HOMA for interacting system ($HOMA_{int}$) and that of free one, $HOMA^0$: $\Delta HOMA = HOMA_{int} - HOMA^0$**.** Background denotes the same type of interactions.

Table S4 Changes of HOMA values for adenine complexes with Li^+

	E_{tot}/ kcal/mol	HOMA6	HOMA5	$HOMA_{tot}$	ΔHOMA6	ΔHOMA5	$\Delta HOMA_{tot}$
1H adenine		**0.797**	**0.857**	**0.862**			
(N3,N9)···Li^+	-67.50	0.898	0.940	0.915	0.101	0.083	0.053
(N7,N10)···Li^+	-51.17	0.774	0.830	0.849	-0.023	-0.027	-0.013
3H adenine		**0.920**	**0.923**	**0.928**			
(N1,N10)···Li^+	-41.45	0.791	0.752	0.838	-0.129	-0.171	-0.090
(N7,N10)···Li^+	-52.57	0.916	0.907	0.928	-0.004	-0.016	0.000
N9···Li^+	-52.41	0.920	0.894	0.900	0.000	-0.029	-0.028
7H adenine		**0.982**	**0.857**	**0.923**			
(N1,N10)···Li^+	-47.60	0.923	0.825	0.903	-0.059	-0.032	-0.020
(N3,N9)···Li^+	-65.73	0.970	0.889	0.927	-0.012	0.032	0.004
9H adenine		**0.984**	**0.869**	**0.926**			
(N1,N10)···Li^+	-49.18	0.959	0.861	0.924	-0.025	-0.008	-0.002
N3···Li^+	-45.70	0.951	0.872	0.907	-0.033	0.003	-0.019
(N7,N10)···Li^+	-50.97	0.986	0.882	0.934	0.002	0.013	0.008

Table S5 Changes of HOMA values for adenine complexes with Na^+

	E_{tot}/ kcal/mol	HOMA6	HOMA5	$HOMA_{tot}$	ΔHOMA6	ΔHOMA5	$\Delta HOMA_{tot}$
1H adenine		**0.797**	**0.857**	**0.862**			
(N3,N9)···Na^+	-51.39	0.888	0.933	0.911	0.091	0.076	0.049
(N7,N10)···Na^+	-32.84	0.741	0.778	0.829	-0.056	-0.079	-0.033
3H adenine		**0.920**	**0.923**	**0.928**			
(N1,N10)···Na^+	-25.04	0.838	0.804	0.869	-0.082	-0.119	-0.059
(N7,N10)···Na^+	-34.90	0.934	0.914	0.938	0.014	-0.009	0.010
N9···Na^+	-36.05	0.921	0.909	0.909	0.001	-0.014	-0.019
7H adenine		**0.982**	**0.857**	**0.923**			
(N1,N10)···Na^+	-29.88	0.937	0.952	0.910	-0.045	-0.024	-0.013
(N3,N9)···Na^+	-49.82	0.976	0.976	0.931	-0.006	0.033	0.008
9H adenine		**0.984**	**0.869**	**0.926**			
(N1,N10)···Na^+	-32.18	0.974	0.871	0.930	-0.010	0.002	0.004
N3···Na^+	-30.26	0.962	0.871	0.913	-0.022	0.002	-0.013
(N7,N10)···Na^+	-32.94	0.988	0.878	0.934	0.004	0.009	0.008

Table S6 Charge transfer characteristic for adenine complexes [(a)] with HF/F^-

Tautomer	Interaction	Charge transfer/ au.		Interaction	Charge transfer/ au.
1H adenine	$N1^-\cdots HF$	0.142	**3H adenine**	N1···HF	0.082
	N3···HF	0.069		$N3^-\cdots HF$	0.117
	N7···HF	0.101		N7···HF	0.097
	N9···HF	0.083		N9···HF	0.086
	N10···HF	0.067		N10···HF	0.057
	$H14\cdots F^{-(b)}$	0.162		$H14\cdots F^{-(b)}$	0.133
	$H15\cdots F^{-(b)}$	0.110		$H15\cdots F^{-(b)}$	0.121
7H adenine	N1···HF	0.090	**9H adenine**	N1···HF	0.092
	N3···HF	0.076		N3···HF	0.083
	$N7^-\cdots HF$	0.163		N7···HF	0.082
	N9···HF	0.072		$N9^-\cdots HF$	0.127
	N10···HF	0.081		N10···HF	0.062
	$H14\cdots F^{-(b)}$	0.138		$H14\cdots F^{-(b)}$	0.142
	$H15\cdots F^{-(b)}$	0.163		$H15\cdots F^{-(b)}$	0.136

[(a)] The electron transfer occurs from the molecule of adenine into the second part of the complex (HF). [(b)] Proton transfer takes place leading to $N10^-\cdots HF$ interaction.

Table S7 Charge transfer characteristic for adenine complexes with Li^+ and Na^+

Tautomer	Interaction	Charge transfer/ au.	Interaction	Charge transfer/ au.
1H adenine	$(N3,N9)\cdots Li^+$	0.065	$(N3,N9)\cdots Na^+$	0.072
	$(N7,N10)\cdots Li^+$	0.073	$(N7,N10)\cdots Na^+$	0.079
3H adenine	$(N1,N10)\cdots Li^+$	0.070	$(N1,N10)\cdots Na^+$	0.071
	$(N7,N10)\cdots Li^+$	0.075	$(N7,N10)\cdots Na^+$	0.077
	$N9\cdots Li^+$	0.056	$N9\cdots Na^+$	0.065
7H adenine	$(N1,N10)\cdots Li^+$	0.070	$(N1,N10)\cdots Na^+$	0.078
	$(N3,N9)\cdots Li^+$	0.065	$(N3,N9)\cdots Na^+$	0.073
9H adenine	$(N1,N10)\cdots Li^+$	0.071	$(N1,N10)\cdots Na^+$	0.074
	$N3\cdots Li^+$	0.056	$N3\cdots Na^+$	0.064
	$(N7,N10)\cdots Li^+$	0.074	$(N7,N10)\cdots Na^+$	0.078

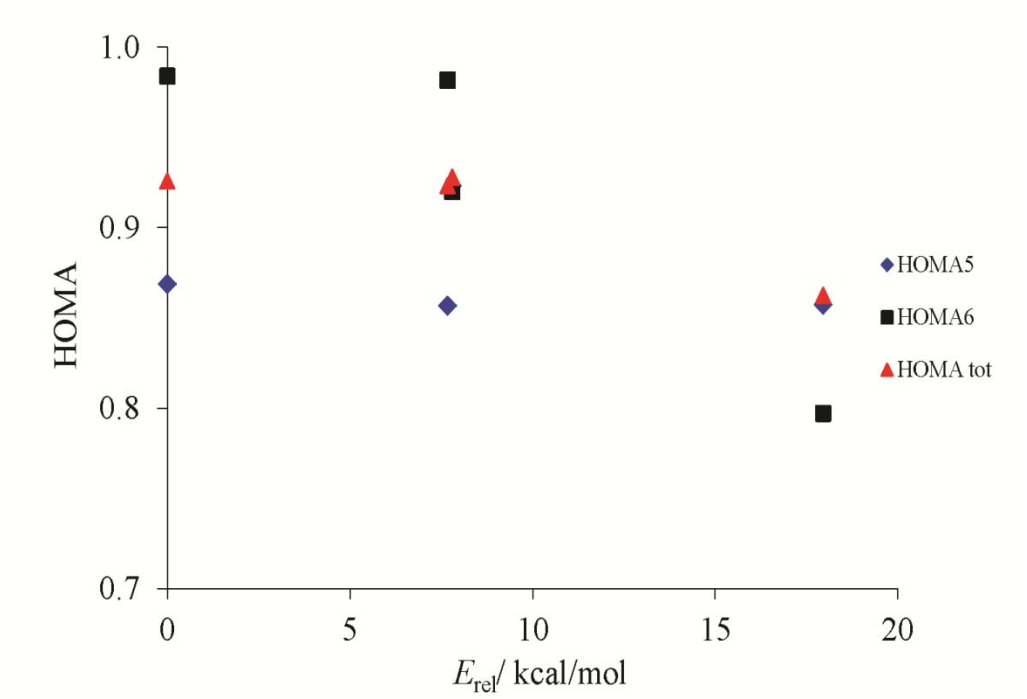


Fig. S1 Dependences of HOMA values on relative energy, E_{rel}, of free adenine tautomers

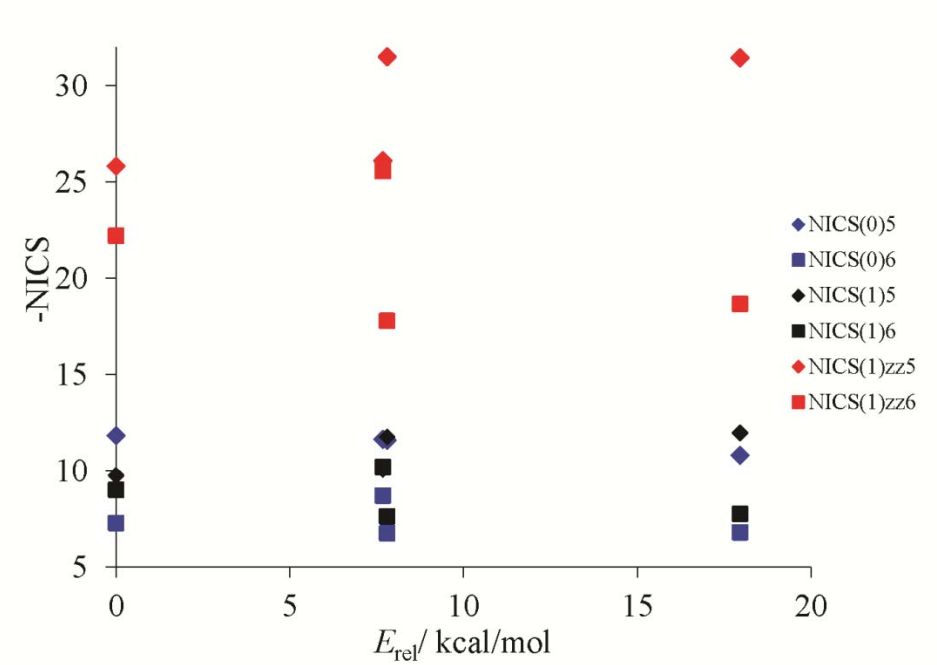


Fig. S2 Dependences of NICS values on relative energy, E_{rel}, of free tautomers of adenine

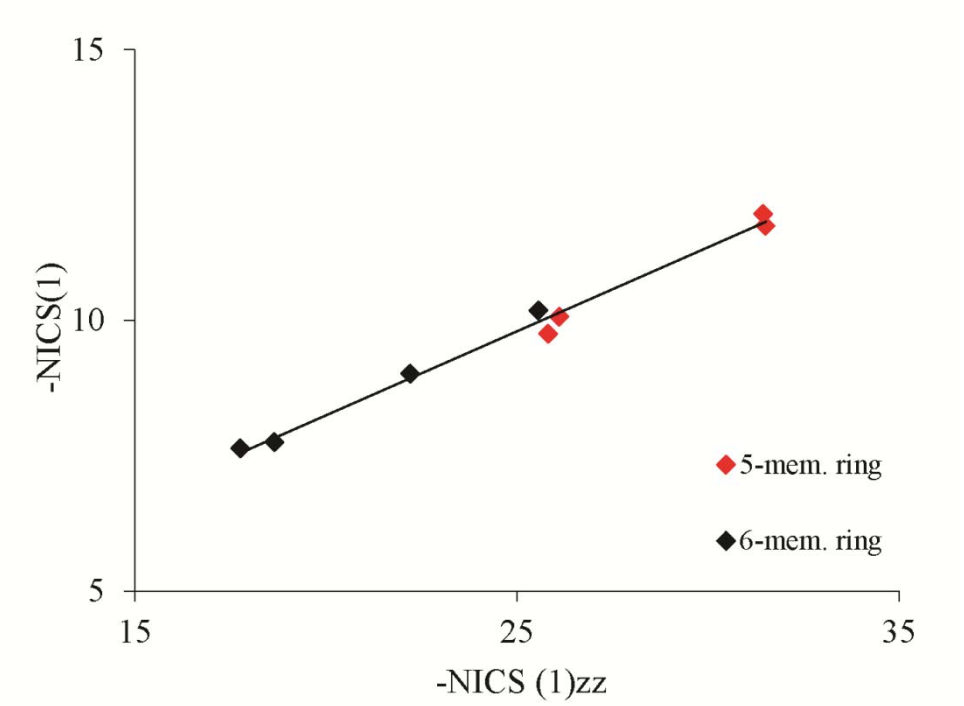


Fig. S3 Interrelations between NICS(1) and NICS(1)zz for five- and six-membered rings of adenine tautomers and for all points considered together

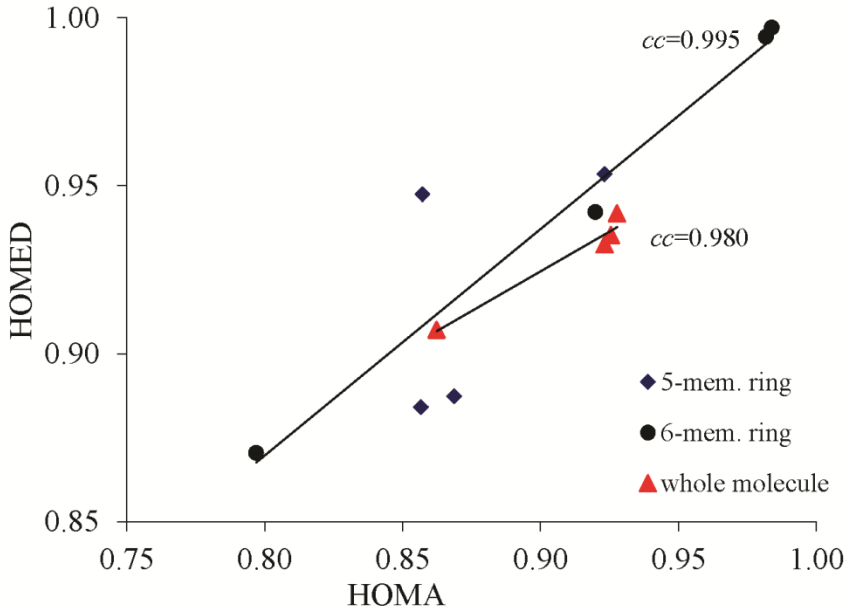
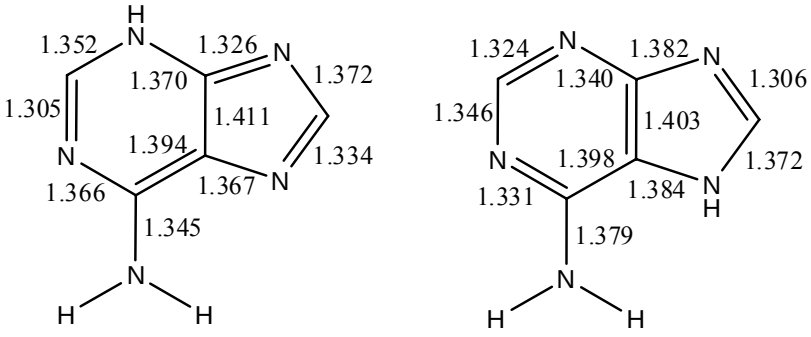


Fig. S4 Correlations between HOMA and HOMED values for free adenine tautomers



3H adenine 7H adenine

Fig. S5 Optimized geometries of 3H and 7H adenine tautomers

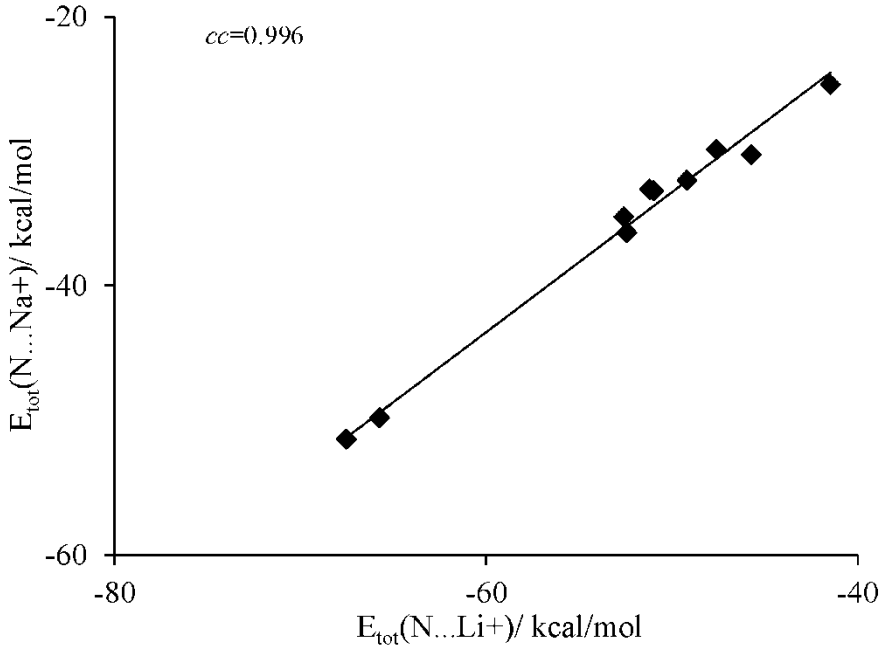


Fig. S6 Correlation between total energies of N···Na^+ and N···Li^+ interactions

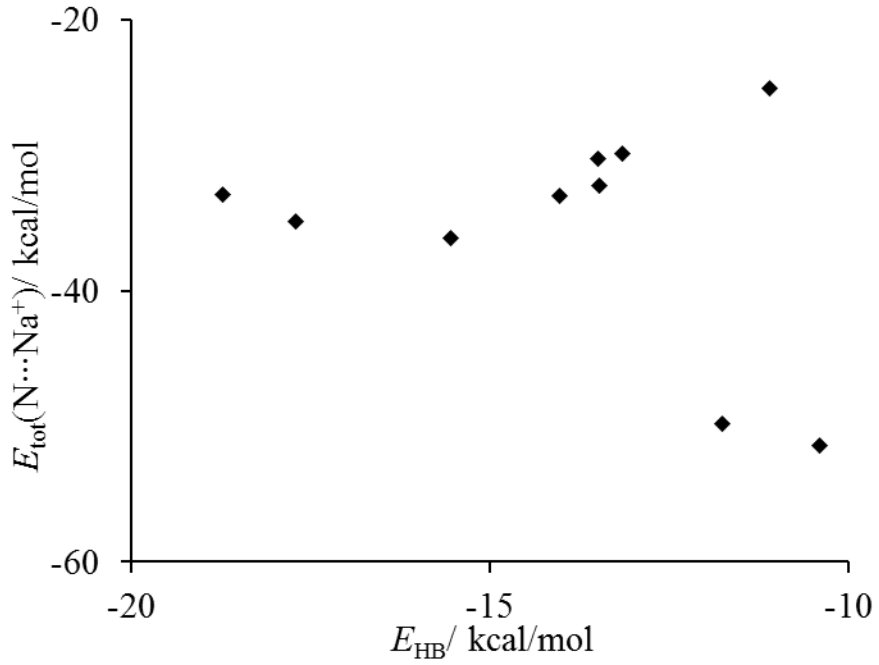


Fig. S7 Dependence of total energy of interaction N···Na^+ on total energy of interaction N···HF

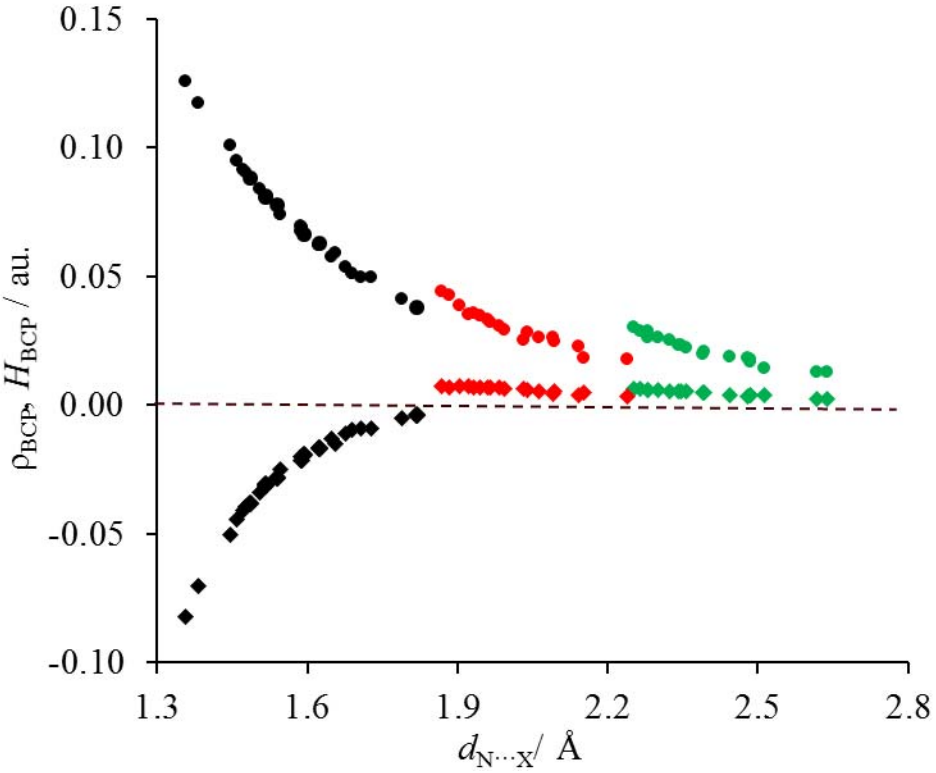


Fig. S8 Dependencies of AIM characteristics at BCP for interactions of adenine tautomers with HF (black); Li^+ (red); and Na^+ (green): diamonds – H_{BCP}; circles – ρ_{BCP}, on interatomic distance, $d_{N\cdots X}$, X=H, Li, Na

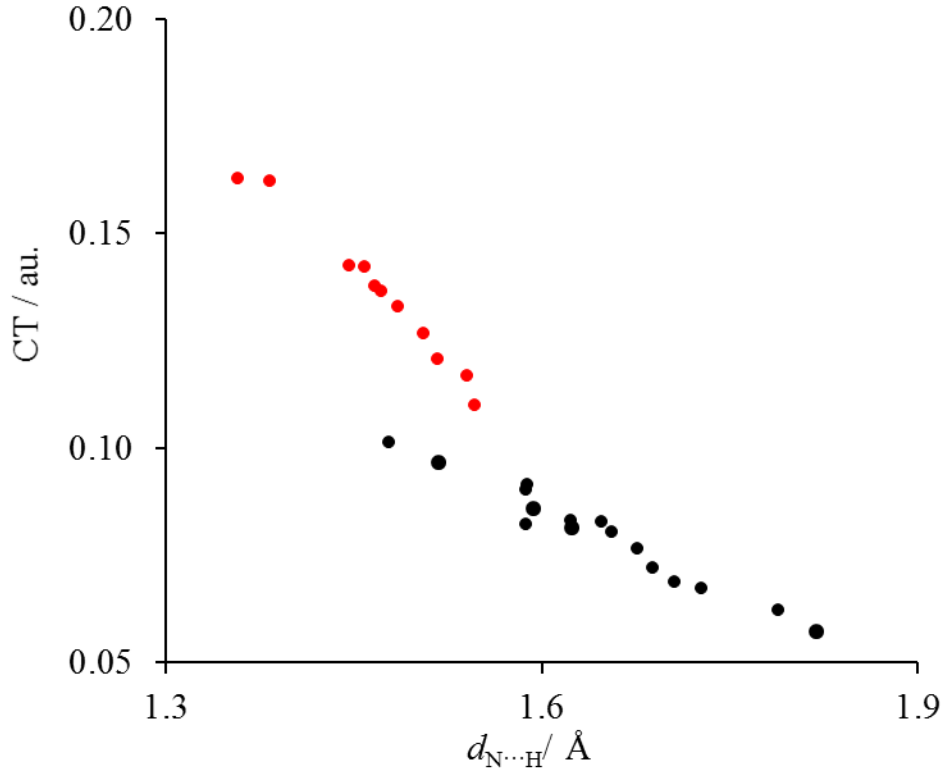


Fig. S9 Relationship between CT and interatomic distance, $d_{N\cdots H}$, for neutral (black) and charge-assisted (red) H-bond interactions of adenine tautomers