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Structural grounds for the 2-aminopurine mutagenicity: A novel insight into the old problem of the replication errors

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Table S1. Electron-topological, structural, vibrational and energetic characteristics of the intermolecular H-bonds in the investigated complexes and TSs of their tautomerisation involving DNA bases and 2AP (see Fig. 1), their energetic and polar characteristics obtained at the B3LYP/6-311++G(d,p) level of theory (ε=1).

Base pair/complex/TS	AH···B H-bond	ρ^a	$\Delta\rho^b$	$100\cdot\varepsilon^c$	$d_{A\cdots B}{}^d$	$d_{H\cdots B}{}^e$	$\Delta d_{AH}{}^f$	∠AH···B^g	$\Delta\nu^h$	$E_{AH\cdots B}{}^i$	ΔG^j	μ^k
2AP·H$_2$O	OH···N1	0.031	0.091	3.70	2.836	1.930	0.018	152.4	353.6	5.84	0.00	3.15
	N2H···O	0.019	0.072	8.19	2.954	2.070	0.007	144.5	118.0	2.91		
TS$_{2AP\cdot H2O\leftrightarrow 2AP^*\cdot H2O}$	N1H···O	0.096	0.126	3.39	2.478	1.429	-	150.4	-	-	22.05	4.82
2AP*·H$_2$O	N1H···O	0.029	0.103	4.75	2.816	1.893	0.016	147.9	263.5	4.93	17.41	3.28
	OH···N2	0.040	0.102	4.59	2.727	1.823	0.030	149.9	561.7	7.54		
A·H$_2$O	N6H···O	0.020	0.076	5.93	2.917	2.044	0.009	142.6	149.4	3.45	0.00	2.94
	OH···N1	0.031	0.090	3.82	2.829	1.933	0.019	150.6	359.8	5.90		
TS$_{A\cdot H2O\leftrightarrow A^*\cdot H2O}$	N6$^+$H···O$^-$	0.129	0.020	3.11	2.438	1.315	0.193	151.1	1728.2	13.56	18.40	4.65
	N1$^+$H···O$^-$	0.104	0.111	3.31	2.461	1.399	0.137	149.5	1549.6	12.82		
A*·H$_2$O	OH···N6	0.036	0.098	4.27	2.755	1.863	0.026	148.6	481.1	6.93	9.77	3.28
	N1H···O	0.027	0.097	4.26	2.831	1.923	0.013	145.8	220.9	4.44		
2AP·T(WC)	C6H···O4	0.005	0.016	2.18	3.879	2.792	0.0004	132.0	-3.1	0.90*	0.00	3.15
	N3H···N1	0.040	0.095	6.42	2.876	1.832	0.032	179.3	567.1	7.58		
	N2H···O2	0.023	0.082	5.68	2.998	1.982	0.010	174.9	171.4	3.78		
TS$^{2AP+\cdot T-}_{2AP\cdot T(WC)\leftrightarrow 2AP\cdot T^*(w)}$	N1$^+$H···O4$^-$	0.033	0.099	7.55	2.918	1.869	0.036	143.2	567.7	4.48	15.48	6.45
	N1$^+$H···N3$^-$	0.025	0.081	26.93	3.064	2.015	0.036	146.1	567.7	3.10		
	N2$^+$H···N3$^-$	0.022	0.070	3.88	3.119	2.093	0.013	143.7	296.8	3.09		
	N2$^+$H···O2$^-$	0.016	0.053	34.47	3.201	2.175	0.019	151.8	296.8	2.20		
2AP·T*(w)	O4H···N1	0.057	0.097	5.05	2.698	1.678	0.050	169.2	954.1	9.98	7.33	1.52
	N2H···N3	0.029	0.085	7.39	2.987	1.965	0.016	168.9	295.0	5.27		
TS$_{2AP\cdot T^*(w)\leftrightarrow 2AP^*\cdot T(w)}$	N1H···O4	0.060	0.141	3.37	2.667	1.604	-	178.9	-	18.63*	14.46	3.39
2AP*·T(w)	N1H···O4	0.038	0.122	3.58	2.804	1.770	0.023	180.0	411.1	6.36	15.28	2.88
	N3H···N2	0.049	0.096	6.42	2.810	1.748	0.049	175.0	828.4	9.27		
A·T(WC)	N6H···O4	0.026	0.093	4.39	2.946	1.926	0.014	173.5	238.7	4.65	0.00	1.88
	N3H···N1	0.040	0.093	6.49	2.886	1.841	0.032	178.8	567.5	7.58		
	C2H···O2	0.004	0.014	3.40	3.975	2.890	0.0002	132.3	-4.8	0.74*		
TS$^{A+\cdot T-}_{A\cdot T(WC)\leftrightarrow A\cdot T^*(w)}$	N6$^+$H···O4$^-$	0.023	0.097	6.47	2.974	1.953	0.012	140.6	188.0	4.01	20.28	7.77
	N1$^+$H···O4$^-$	0.055	0.128	0.19	2.723	1.656	0.053	153.6	1668.9	13.32		
	C2$^+$H···N3$^-$	0.009	0.030	57.50	3.751	2.665	0.002	113.5	-28.1	1.60*		
A·T*(w)	N6H···N3	0.017	0.056	10.90	3.018	2.240	0.013	132.0	194.5	4.10	17.47	4.16
	O4H···N6	0.028	0.078	6.20	2.930	1.963	0.016	166.1	322.7	5.55		
TS$^{2AP+\cdot T-}_{2AP\cdot T(WC)\leftrightarrow 2AP\cdot T^*O2(w)}$	C6H···N3	0.012	0.058	24.35	3.125	2.504	0.001	115.1	-11.3	2.09*	22.47	9.59
	N1H···O2	0.057	0.058	0.74	2.666	1.641	0.054	159.4	840.4	9.34		
	N2H···O2	0.019	0.058	6.61	2.906	2.047	0.009	140.6	136.6	3.24		
2AP·T*$_{O2}$(w)	C6H···N3	0.011	0.058	0.43	3.309	2.511	0.000	129.4	-10.4	1.71*	17.10	7.05
	O2H···N1	0.062	0.058	5.13	2.666	1.647	0.054	174.9	1033.7	10.40		
TS$^{A+\cdot T-}_{A\cdot T(WC)\leftrightarrow A+\cdot T-(w)}$	N6$^+$H···O4$^-$	0.020	0.065	16.30	3.102	2.070	0.024	153.2	377.5	2.82	16.72	6.77
	N6$^+$H···N3$^-$	0.023	0.075	0.89	3.097	2.064	0.024	140.7	377.5	3.24		
	N1$^+$H···N3$^-$	0.022	0.075	53.95	3.136	2.090	0.032	139.6	503.7	2.55		
	N1$^+$H···O2$^-$	0.034	0.101	4.19	2.893	1.847	0.032	150.4	503.7	4.56		
A$^+\cdot$T$^-$(w)	N6$^+$H···N3$^-$	0.069	0.086	5.82	2.693	1.609	0.078	173.8	1314.2	11.78	12.43	6.86
	N1$^+$H···O2$^-$	0.076	0.140	3.66	2.602	1.508	0.080	180.0	1261.5	11.53		
TS$_{A+\cdot T-(w)\leftrightarrow A\cdot T^*O2(w)}$	N6H···N3	0.047	0.099	6.37	2.800	1.765	-	168.0	-	8.57*	10.73	5.63
A·T*$_{O2}$(w)	N6H···N3	0.034	0.088	1.71	2.944	1.915	0.020	167.1	391.9	6.19	10.91	3.96
	O2H···N1	0.071	0.081	0.86	2.644	1.608	0.067	171.9	1239.6	11.43		

Table S1 *(continued).*

Base pair/TS	AH···B/ AH···HB H-bond/ N···N van der Waals contact	ρ	$\Delta\rho$	$100\cdot\varepsilon$	$d_{A\cdots B}$/ $d_{N\cdots N}$	$d_{H\cdots B}$/ $d_{N\cdots N}$	Δd_{AH}	∠AH···B	$\Delta\nu$	$E_{AH\cdots B}$/ $E_{AH\cdots HB}$/ $E_{N\cdots N}$	ΔG	μ
A*·2AP(WC)	C6H···N6	0.013	0.039	5.58	3.332	2.388	0.002	144.2	22.3	2.04*	0.00	4.57
	N1H···N1	0.029	0.082	7.01	2.991	1.961	0.019	175.2	346.1	5.77		
	C2H···HN2	0.001	0.005	75.42	3.668	2.987	0.0008	125.7	14.4	0.17*		
$TS_{A^*\cdot 2AP(WC)\leftrightarrow A^*\cdot 2APsyn}$	C6H···O6	0.010	0.029	2.16	3.554	2.501	0.0025	162.6	26.8	1.52*	6.54	4.78
$A^*\cdot 2AP_{syn}$	C6H···N6	0.012	0.036	5.36	3.413	2.412	0.001	152.4	9.7	1.89*	-0.83	4.93
	N1H···N7	0.027	0.080	6.02	3.009	1.984	0.017	174.3	295.2	5.27		
A*·A(WC)	N6H···N6	0.035	0.091	7.19	2.918	1.885	0.028	176.3	491.5	7.01	0.00	1.75
	N1H···N1	0.034	0.087	6.76	2.943	1.904	0.030	179.0	474.6	6.88		
$TS_{A^*\cdot A(WC)\leftrightarrow A^*\cdot Asyn(TF)}$	N6H···N6	0.028	0.082	3.34	2.960	1.985	0.021	157.5	362.0	5.92	8.09	5.46
	N1H···N6	0.011	0.033	40.58	3.317	2.447	0.004	143.3	63.7	1.61		
	N1···N6	0.002	0.008	67.50	3.790	-	-	-	-	0.39*		
$A^*\cdot A_{syn}$(TF)	N6H···N6	0.032	0.098	7.17	2.937	1.921	0.023	168.9	410.4	6.35	0.56	7.96
	N1H···N7	0.032	0.093	5.99	2.959	1.929	0.022	173.5	389.1	6.17		
G*·2AP(w)	O6H···N1	0.049	0.100	5.14	2.728	1.735	0.038	168.4	737.7	8.72	-1.33	4.58
	N2H···N1	0.026	0.077	7.43	3.029	2.016	0.014	171.3	271.8	5.02		
$TS^{G^{-}\cdot 2AP^{+}}_{G^*\cdot 2AP(WC)\leftrightarrow G\cdot 2AP(w)}$	$C6^{+}H\cdots O6^{-}$	0.013	0.049	67.40	2.961	2.380	0.002	112.0	10.5	2.66*	16.70	10.62
	$N1^{+}H\cdots O6^{-}$	0.028	0.092	26.10	2.754	1.963	0.037	129.7	575.9	3.48		
	$N1^{+}H\cdots N1^{-}$	0.031	0.088	6.86	2.910	1.915	0.037	156.9	575.9	4.15		
	$N2^{+}H\cdots N1^{-}$	0.014	0.045	8.67	3.166	2.318	0.011	139.9	181.3	2.17		
	$N2^{+}H\cdots N2^{-}$	0.013	0.044	9.18	3.240	2.286	0.011	155.5	181.3	1.76		
G·2AP(WC)	C6H···O6	0.010	0.029	2.90	3.366	2.470	0.0009	138.9	0.1	1.70*	0.00	7.72
	N1H···N1	0.033	0.088	6.76	2.948	1.916	0.021	176.2	378.6	6.07		
	N2H···N2	0.008	0.026	110.77	3.400	2.654	0.003	130.7	54.1	1.24		
$TS_{G\cdot 2AP(WC)\leftrightarrow G\cdot 2APsyn}$	C6H···O6	0.009	0.027	3.61	3.484	2.491	0.001	151.2	9.1	1.56*	9.56	7.67
	N1H···C6	0.004	0.013	137.20	3.762	2.907	0.000	142.5	5.5	0.58*		
$G\cdot 2AP_{syn}$	C6H···O6	0.012	0.039	4.75	3.298	2.340	-0.0003	146.0	-13.8	2.12*	0.60	7.92
	N1H···N7	0.027	0.079	5.85	3.021	1.992	0.017	179.5	293.1	5.25		
G·A(WC)	N6H···O6	0.032	0.109	3.79	2.866	1.842	0.019	176.6	336.2	5.68	0.00	5.21
	N1H···N1	0.032	0.084	6.64	2.972	1.936	0.024	178.9	429.1	6.51		
	C2H···HN2	0.004	0.014	33.40	3.153	2.469	0.0000	124.6	-0.5	0.68*		
$TS^{G^{-}\cdot A^{+}}_{G\cdot A(WC)\leftrightarrow G^*\cdot A(w)}$	$N6^{+}H\cdots O6^{-}$	0.048	0.162	5.72	2.605	1.648	0.034	150.2	551.2	7.46	17.01	9.26
	$N1^{+}H\cdots O6^{-}$	0.029	0.091	10.22	2.800	1.946	0.033	136.4	512.3	4.21		
	$N1^{+}H\cdots N1^{-}$	0.023	0.072	18.76	3.011	2.045	0.033	152.1	512.3	2.96		
G*·A(w)	N6H···O6	0.012	0.048	5.41	3.043	2.246	0.004	134.6	64.6	1.64	3.76	2.39
	O6H···N1	0.047	0.103	4.89	2.695	1.755	0.034	154.5	655.8	8.19		
$TS_{G\cdot A(WC)\leftrightarrow G\cdot Asyn(TF)}$	N6H···O6	0.024	0.083	3.30	2.942	1.986	0.015	154.7	249.1	4.77	8.39	6.71
	N1H···N6	0.011	0.035	36.44	3.296	2.425	0.003	143.3	59.6	1.46		
	N1···N7	0.002	0.009	104.95	3.802	-	-	-	-	0.40*		
$G\cdot A_{syn}$	N6H···O6	0.029	0.104	2.85	2.886	1.874	0.016	169.9	276.9	5.08	0.76	7.93
	N1H···N7	0.032	0.087	5.50	2.958	1.926	0.022	175.6	383.8	6.12		
C*·2AP(WC)	C6H···N4	0.007	0.020	3.62	3.804	2.717	0.0006	133.6	-0.5	1.10*	-	2.70
	N3H···N1	0.039	0.094	6.50	2.883	1.841	0.030	178.9	543.4	7.40		
	N2H···O2	0.022	0.082	5.65	3.001	1.985	0.010	174.6	170.3	3.77		
C*·A(WC)	N6H···N4	0.029	0.082	7.63	2.983	1.959	0.021	173.8	371.7	6.01	-	3.10
	N3H···N1	0.040	0.093	6.59	2.895	1.852	0.031	178.9	551.6	7.46		
	C2H···O2	0.005	0.017	1.48	3.628	2.798	0.0001	133.1	−5.9	0.96*		

[a]The electron density at the (3,-1) BCP of the H-bond, a.u.; [b]The Laplacian of the electron density at the (3,-1) BCP of the H-bond, a.u.; [c]The ellipticity at the (3,-1) BCP of the H-bond; [d]The distance between the A (H-bond donor) and B (H-bond acceptor) atoms of the AH···B H-bond, Å; [e]The distance between the H and B atoms of the AH···B H-bond, Å; [f]The elongation of the H-bond donating group AH upon the AH···B H-bonding, Å; [g]The H-bond angle, degree; [h]The redshift of the stretching vibrational mode ν(AH) of the AH H-bonded group, cm^{-1}; [i]Energy of the H-bonds, calculated by Iogansen's [1] or Espinose-Molins-Lecomte (EML) [2,3] (marked with an asterisk) formulas, $kcal\cdot mol^{-1}$; [j]The relative Gibbs free energy of the complex obtained at the MP2/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level of theory under normal conditions (ε=1), $kcal\cdot mol^{-1}$; [k]The dipole moment of the complex, D.

Table S2. Energetic and kinetic characteristics of the (**a**) 2AP↔2AP*, (**b**) A↔A*, (**c**) 2AP·H_2O↔2AP*·H_2O and (**d**) A·H_2O↔A*·H_2O tautomerisations obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory in the continuum with ε=1/ε=4.

Level of theory	ΔG^a	ΔE^b	$\Delta\Delta G_{TS}^c$	$\Delta\Delta E_{TS}^d$	$\Delta\Delta G^e$	$\Delta\Delta E^f$	$\tau_{99.9\%}^g$
(a) 2AP↔2AP*							
ε=1 (ν_i=1798.9*i* cm^{-1})							
MP2/6-311++G(2df,pd)	21.80	21.93	46.61	50.09	24.81	28.1	$4.46\cdot10^{5}$
MP2/aug-cc-pVDZ	21.69	21.63	47.07	50.55	25.38	28.9	$1.18\cdot10^{6}$
ε=4 (ν_i=1849.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	19.62	19.60	47.16	50.84	27.54	31.2	$4.31\cdot10^{7}$
MP2/aug-cc-pVDZ	19.26	19.24	47.59	51.27	28.33	32.0	$1.64\cdot10^{8}$
(b) A↔A*							
ε=1 (ν_i=1828.5*i* cm^{-1})							
MP2/6-311++G(2df,pd)	14.04	12.27	45.72	47.61	31.68	35.3	$4.81\cdot10^{10}$
MP2/aug-cc-pVDZ	13.60	11.82	46.16	48.05	32.56	36.2	$2.13\cdot10^{11}$
ε=4 (ν_i=1869.9*i* cm^{-1})							
MP2/6-311++G(2df,pd)	11.94	10.90	45.98	48.80	34.03	37.9	$2.47\cdot10^{12}$
MP2/aug-cc-pVDZ	11.49	10.45	46.39	49.22	34.90	38.7	$1.07\cdot10^{13}$
(c) 2AP·H_2O↔2AP*·H_2O							
ε=1 (ν_i=1184.6*i* cm^{-1})							
MP2/6-311++G(2df,pd)	17.48	16.62	22.20	24.22	4.72	7.59	$1.42\cdot10^{-9}$
MP2/aug-cc-pVDZ	17.41	16.55	22.05	24.06	4.63	7.51	$1.23\cdot10^{-9}$
ε=4 (ν_i=906.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	17.00	16.06	22.28	23.58	5.29	7.52	$4.82\cdot10^{-9}$
MP2/aug-cc-pVDZ	16.78	15.84	21.61	22.91	4.83	7.07	$2.24\cdot10^{-9}$
(d) A·H_2O↔A*·H_2O							
ε=1 (ν_i=1198.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	10.00	9.19	18.59	20.79	8.59	11.60	$9.67\cdot10^{-7}$
MP2/aug-cc-pVDZ	9.77	8.96	18.40	20.60	8.63	11.64	$1.03\cdot10^{-6}$
ε=4 (ν_i=693.4*i* cm^{-1})							
MP2/6-311++G(2df,pd)	10.04	8.95	19.28	20.38	9.24	11.43	$4.67\cdot10^{-6}$
MP2/aug-cc-pVDZ	9.74	8.65	18.51	19.61	8.77	10.96	$2.11\cdot10^{-6}$

[a]The Gibbs free energy of the product relatively the reactant of the tautomerisation reaction (T=298.15 K), kcal·mol^{-1}; [b]The electronic energy of the product relatively the reactant of the tautomerisation reaction, kcal·mol^{-1}; [c]The Gibbs free energy barrier for the forward reaction of tautomerisation, kcal·mol^{-1}; [d]The electronic energy barrier for the forward reaction of tautomerisation, kcal·mol^{-1}; [e]The Gibbs free energy barrier for the reverse reaction of tautomerisation, kcal·mol^{-1}; [f]The electronic energy barrier for the reverse reaction of tautomerisation, kcal·mol^{-1}; [g]The time necessary to reach 99.9% of the equilibrium concentration between the reactant and the product of the tautomerisation reaction, s.

Table S3. Energetic and kinetic characteristics of the (**a**) 2AP·T(WC)↔2AP^{+}·T^{-}(w), (**b**) 2AP^{+}·T^{-}(w)↔2AP·T*$_{O2}$(w), (**c**) A·T(WC)↔A^{+}·T^{-}(w), (**d**) A^{+}·T^{-}(w)↔A·T*$_{O2}$(w), (**e**) 2AP·T(WC)↔2AP·T*$_{O2}$(w), (**f**) A·T(WC)↔A·T*$_{O2}$(w), (**g**) 2AP·T(WC)↔2AP·T*(w), (**h**) 2AP·T*(w)↔2AP*·T(w) and (**i**) A·T(WC)↔A·T*(w) tautomerisations *via* the sequential DPT accompanied with structural rearrangements of the bases relative to each other obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory in the continuum with ε=1/ε=4.

Level of theory	ΔG^a	ΔE^b	$\Delta\Delta G_{TS}^c$	$\Delta\Delta E_{TS}^d$	$\Delta\Delta G^e$	$\Delta\Delta E^f$	$\tau_{99.9\%}^g$
(a) 2AP·T(WC)↔2AP^{+}·T^{-}(w)							
ε=4 (ν_i=75.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	15.98	17.68	18.39	18.32	2.41	0.63	$6.43\cdot10^{-11}$
MP2/aug-cc-pVDZ	15.83	17.54	17.95	17.88	2.11	0.34	$3.93\cdot10^{-11}$
(b) 2AP^{+}·T^{-}(w)↔2AP·T*$_{O2}$(w)							
ε=4 (ν_i=737.7*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-2.74	-3.31	-2.55	-0.54	0.19	2.77	$1.00\cdot10^{-14}$
MP2/aug-cc-pVDZ	-1.88	-2.45	-2.02	0.00	-0.13	2.44	$2.38\cdot10^{-14}$
(c) A·T(WC)↔A^{+}·T^{-}(w)							
ε=1 (ν_i=128.5*i* cm^{-1})							
MP2/6-311++G(2df,pd)	12.52	13.44	17.44	16.74	4.92	3.30	$4.48\cdot10^{-9}$
MP2/aug-cc-pVDZ	12.43	13.36	16.72	16.02	4.29	2.66	$1.54\cdot10^{-9}$
ε=4 (ν_i=113.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	10.57	10.91	15.08	14.23	4.51	3.32	$2.24\cdot10^{-9}$
MP2/aug-cc-pVDZ	10.39	10.73	14.41	13.56	4.03	2.83	$9.86\cdot10^{-10}$
(d) A^{+}·T^{-}(w)↔A·T*$_{O2}$(w)							
ε=1 (ν_i=700.3*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-2.11	-2.69	-2.10	-0.74	0.01	1.96	$2.16\cdot10^{-14}$
MP2/aug-cc-pVDZ	-1.52	-2.11	-1.71	-0.34	-0.18	1.77	$4.02\cdot10^{-14}$
ε=4 (ν_i=869.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-0.87	-0.92	-1.34	0.38	-0.47	1.30	$5.63\cdot10^{-14}$
MP2/aug-cc-pVDZ	-0.19	-0.24	-0.73	0.99	-0.54	1.23	$1.12\cdot10^{-13}$
(e) 2AP·T(WC)↔2AP·T*$_{O2}$(w)							
ε=1 (ν_i=76.1*i* cm^{-1})							
MP2/6-311++G(2df,pd)	16.41	17.22	22.95	22.46	6.54	5.24	$6.94\cdot10^{-8}$
MP2/aug-cc-pVDZ	17.10	17.91	22.47	21.97	5.36	4.06	$9.52\cdot10^{-9}$
ε=4 (ν_i=75.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	13.24	14.38	18.39	18.32	5.15	3.94	$6.59\cdot10^{-9}$
MP2/aug-cc-pVDZ	13.95	15.09	17.95	17.88	4.00	2.79	$9.43\cdot10^{-10}$
(f) A·T(WC)↔A·T*$_{O2}$(w)							
ε=1 (ν_i=128.5*i* cm^{-1})							
MP2/6-311++G(2df,pd)	10.41	10.75	17.44	16.74	7.03	5.99	$1.58\cdot10^{-7}$
MP2/aug-cc-pVDZ	10.91	11.25	16.72	16.02	5.81	4.77	$2.02\cdot10^{-8}$
ε=4 (ν_i=113.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	9.70	9.99	15.08	14.23	5.38	4.24	$9.73\cdot10^{-9}$
MP2/aug-cc-pVDZ	10.19	10.48	14.41	13.56	4.22	3.07	$1.36\cdot10^{-9}$
(g) 2AP·T(WC)↔2AP·T*(w)							
ε=1 (ν_i=134.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	8.17	7.88	19.30	18.17	11.13	10.29	$1.59\cdot10^{-4}$
MP2/aug-cc-pVDZ	8.62	8.33	18.66	17.53	10.04	9.21	$2.53\cdot10^{-5}$
ε=4 (ν_i=112.3*i* cm^{-1})							
MP2/6-311++G(2df,pd)	6.93	7.39	16.16	15.41	9.23	8.01	$6.48\cdot10^{-6}$
MP2/aug-cc-pVDZ	7.33	7.79	15.48	14.72	8.15	6.93	$1.04\cdot10^{-6}$
(h) 2AP·T*(w)↔2AP*·T(w)							
ε=1 (ν_i=1018.0*i* cm^{-1})							
MP2/6-311++G(2df,pd)	8.17	7.84	7.36	9.48	-0.81	1.64	$1.46\cdot10^{-13}$
MP2/aug-cc-pVDZ	7.83	7.50	7.02	9.14	-0.81	1.64	$1.46\cdot10^{-13}$
ε=4 (ν_i=1129.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	8.35	7.43	7.53	9.07	-0.82	1.64	$1.29\cdot10^{-13}$
MP2/aug-cc-pVDZ	7.90	6.98	7.10	8.64	-0.80	1.66	$1.33\cdot10^{-13}$
(i) A·T(WC)↔A·T*$_{\downarrow}$(w)							
ε=1 (ν_i=99.7*i* cm^{-1})							
MP2/6-311++G(2df,pd)	12.47	14.23	20.82	20.95	8.35	6.73	$1.47\cdot10^{-6}$
MP2/aug-cc-pVDZ	13.08	14.84	20.28	20.41	7.20	5.57	$2.09\cdot10^{-7}$
ε=4 (ν_i=79.4*i* cm^{-1})							
MP2/6-311++G(2df,pd)	10.01	11.79	16.48	16.86	6.47	5.07	$6.13\cdot10^{-8}$
MP2/aug-cc-pVDZ	10.69	12.47	16.03	16.42	5.34	3.94	$9.20\cdot10^{-9}$

See definitions in Table S2.

Table S4. Energetic and kinetic characteristics of the (**a**) A*·2AP(WC)↔A*·2AP$_{syn}$, (**b**) A*·A(WC)↔A*·A$_{syn}$(TF), (**c**) G*·2AP(w)↔G·2AP(WC), (**d**) G·2AP(WC)↔G·2AP$_{syn}$, (**e**) G*·A(w)↔G·A(WC) and (**f**) G·A(WC)↔G·A$_{syn}$ tautomerisations *via* the sequential DPT and conformational transitions obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory in the continuum with ε=1/ε=4.

Level of theory	ΔG	ΔE	$\Delta\Delta G_{TS}$	$\Delta\Delta E_{TS}$	ΔΔG	ΔΔE	$\tau_{99.9\%}$
(a) A*·2AP(WC)↔A*·2AP$_{syn}$							
ε=1 (ν_i=18.0*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-0.94	-0.70	5.59	7.60	6.53	8.30	$1.17\cdot10^{-8}$
MP2/aug-cc-pVDZ	-0.83	-0.59	6.54	8.55	7.37	9.14	$5.59\cdot10^{-8}$
ε=4 (ν_i=6.4*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-0.62	-0.19	4.02	6.34	4.64	6.53	$7.34\cdot10^{-10}$
MP2/aug-cc-pVDZ	-0.49	-0.07	5.13	7.45	5.62	7.52	$4.49\cdot10^{-9}$
(b) A*·A(WC)↔A*·A$_{syn}$(TF)							
ε=1 (ν_i=15.8*i* cm^{-1})							
MP2/6-311++G(2df,pd)	0.54	1.22	7.50	7.50	6.96	6.29	$1.01\cdot10^{-7}$
MP2/aug-cc-pVDZ	0.56	1.23	8.09	8.09	7.53	6.85	$2.66\cdot10^{-7}$
ε=4 (ν_i=8.1*i* cm^{-1})							
MP2/6-311++G(2df,pd)	0.40	0.35	4.78	6.90	4.38	6.55	$1.20\cdot10^{-9}$
MP2/aug-cc-pVDZ	0.44	0.38	5.68	7.80	5.25	7.42	$5.32\cdot10^{-9}$
(c) G*·2AP(w)↔G·2AP(WC)							
ε=1 (ν_i=130.1*i* cm^{-1})							
MP2/6-311++G(2df,pd)	2.06	1.80	19.64	18.19	17.58	16.38	8.29
MP2/aug-cc-pVDZ	1.33	1.07	18.04	16.58	16.70	15.51	1.77
ε=4 (ν_i=104.6*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-0.47	-0.36	13.74	13.05	14.21	13.41	$9.07\cdot10^{-3}$
MP2/aug-cc-pVDZ	-1.20	-1.09	12.30	11.61	13.50	12.71	$1.03\cdot10^{-3}$
(d) G·2AP(WC)↔G·2AP$_{syn}$							
ε=1 (ν_i=17.7*i* cm^{-1})							
MP2/6-311++G(2df,pd)	0.27	1.18	7.23	9.31	6.96	8.13	$8.70\cdot10^{-8}$
MP2/aug-cc-pVDZ	0.60	1.51	8.23	10.31	7.63	8.80	$3.22\cdot10^{-7}$
ε=4 (ν_i=6.4*i* cm^{-1})							
MP2/6-311++G(2df,pd)	1.48	1.17	5.93	8.16	4.45	6.99	$1.89\cdot10^{-9}$
MP2/aug-cc-pVDZ	1.64	1.33	7.26	9.49	5.62	8.16	$1.39\cdot10^{-8}$
(e) G*·A(w)↔G·A(WC)							
ε=1 (ν_i=107.2*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-3.27	-5.70	13.60	11.24	16.88	16.94	$9.71\cdot10^{-3}$
MP2/aug-cc-pVDZ	-4.30	-6.73	12.33	9.97	16.64	16.70	$1.22\cdot10^{-3}$
ε=4 (ν_i=84.5*i* cm^{-1})							
MP2/6-311++G(2df,pd)	-4.00	-6.03	9.51	7.17	13.51	13.20	$1.04\cdot10^{-5}$
MP2/aug-cc-pVDZ	-4.87	-6.90	8.42	6.08	13.29	12.98	$1.65\cdot10^{-6}$
(f) G·A(WC)↔G·A$_{syn}$							
ε=1 (ν_i=20.7*i* cm^{-1})							
MP2/6-311++G(2df,pd)	0.73	0.55	7.80	8.29	7.07	7.75	$1.32\cdot10^{-7}$
MP2/aug-cc-pVDZ	0.76	0.58	8.39	8.89	7.64	8.31	$3.47\cdot10^{-7}$
ε=4 (ν_i=14.4*i* cm^{-1})							
MP2/6-311++G(2df,pd)	0.26	-0.06	6.55	7.13	6.30	7.20	$2.81\cdot10^{-8}$
MP2/aug-cc-pVDZ	0.30	-0.02	7.41	7.99	7.11	8.01	$1.14\cdot10^{-7}$

See definitions in Table S2.

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