

Supplementary Materials (SM)

Solvent effect on the stability and reverse substituent effect in nitropurine tautomers.

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Table S1. The cSAR(NO₂) values for C2-, C6-, C8-NO₂ substituted purine tautomers; systems with I-type proximity in bold.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	average
9H	C ₂	-0.0111	-0.0424	-0.0588	-0.0647	-0.0660	-0.0718	-0.0758	-0.0779	-0.0789	-0.0793	0.0682	-0.0627
7H		-0.0107	-0.0440	-0.0620	-0.0686	-0.0700	-0.0766	-0.0811	-0.0836	-0.0847	-0.0852	0.0745	-0.0667
3H		0.0340	0.0271	0.0241	0.0231	0.0229	0.0220	0.0214	0.0211	0.0210	0.0209	0.0131	0.0237
1H		0.0267	0.0191	0.0160	0.0150	0.0148	0.0140	0.0134	0.0132	0.0131	0.0130	0.0137	0.0158
9H	C ₆	-0.0414	-0.0706	-0.0865	-0.0924	-0.0937	-0.0996	-0.1038	-0.1060	-0.1070	-0.1074	0.0661	-0.0908
7H		-0.0530	-0.0656	-0.0714	-0.0733	-0.0737	-0.0755	-0.0766	-0.0772	-0.0775	-0.0776	0.0246	-0.0722
3H		-0.0370	-0.0643	-0.0791	-0.0846	-0.0858	-0.0912	-0.0949	-0.0969	-0.0979	-0.0983	0.0613	-0.0830
1H		-0.0218	-0.0283	-0.0306	-0.0312	-0.0313	-0.0318	-0.0320	-0.0321	-0.0321	-0.0321	0.0104	-0.0303
9H	C ₈	0.0092	-0.0049	-0.0121	-0.0146	-0.0151	-0.0176	-0.0193	-0.0202	-0.0206	-0.0208	0.0300	-0.0136
7H		0.0212	0.0084	0.0018	-0.0007	-0.0012	-0.0036	-0.0053	-0.0062	-0.0066	-0.0068	0.0280	0.0001
3H		-0.0146	-0.0542	-0.0761	-0.0841	-0.0859	-0.0938	-0.0994	-0.1023	-0.1037	-0.1043	0.0896	-0.0819
1H		-0.0117	-0.0480	-0.0773	-0.0859	-0.0878	-0.0964	-0.1024	-0.1056	-0.1071	-0.1077	0.0960	-0.0830
range		0.087	0.098	0.111	0.116	0.117	0.122	0.125	0.127	0.128	0.129	max	0.0340
average		-0.009	-0.031	-0.043	-0.047	-0.048	-0.052	-0.055	-0.056	-0.057	-0.057		
SD		0.026	0.033	0.039	0.041	0.041	0.044	0.045	0.046	0.047	0.047		
range	C ₂	0.045	0.071	0.086	0.092	0.093	0.099	0.103	0.105	0.106	0.106		
	C ₆	0.031	0.042	0.056	0.061	0.062	0.068	0.072	0.074	0.075	0.075	Δ	0.1417
	C ₈	0.036	0.063	0.079	0.085	0.087	0.093	0.097	0.099	0.100	0.101		
average	C ₂	0.010	-0.010	-0.020	-0.024	-0.025	-0.028	-0.031	-0.032	-0.032	-0.033		
	C ₆	-0.038	-0.057	-0.067	-0.070	-0.071	-0.075	-0.077	-0.078	-0.079	-0.079		
	C ₈	0.001	-0.025	-0.041	-0.046	-0.047	-0.053	-0.057	-0.059	-0.060	-0.060		

Table S2. The cSAR(NO₂) values for C2-, C6-, C8-NO₂ substituted purine tautomers, the nitro group 90° rotated, systems with I-type proximity in bold.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	average
9H	C2	0.0018	-0.0249	-0.0379	-0.0425	-0.0434	-0.0478	-0.0508	-0.0523	-0.0530	-0.0533	0.0551	-0.0404
7H		-0.0013	-0.0303	-0.0449	-0.0501	-0.0512	-0.0563	-0.0598	-0.0616	-0.0625	-0.0628	0.0615	-0.0481
3H		0.0487	0.0466	0.0464	0.0465	0.0465	0.0468	0.0470	0.0472	0.0473	0.0473	0.0023	0.0470
1H		0.0401	0.0388	0.0394	0.0398	0.0399	0.0404	0.0408	0.0410	0.0411	0.0412	0.0023	0.0402
9H	C6	-0.0138	-0.0384	-0.0511	-0.0557	-0.0566	-0.0611	-0.0642	-0.0658	-0.0666	-0.0669	0.0532	-0.0540
7H		-0.0425	-0.0525	-0.0560	-0.0570	-0.0572	-0.0579	-0.0583	-0.0584	-0.0585	-0.0585	0.0161	-0.0557
3H		-0.0035	-0.0266	-0.0384	-0.0427	-0.0436	-0.0478	-0.0506	-0.0522	-0.0529	-0.0532	0.0497	-0.0411
1H		0.0098	0.0094	0.0107	0.0115	0.0117	0.0126	0.0134	0.0138	0.0140	0.0141	0.0047	0.0121
9H	C8	0.0369	0.0307	0.0284	0.0278	0.0277	0.0271	0.0268	0.0266	0.0266	0.0265	0.0104	0.0285
7H		0.0426	0.0369	0.0349	0.0343	0.0342	0.0337	0.0334	0.0333	0.0332	0.0332	0.0094	0.0350
3H		0.0105	-0.0211	-0.0368	-0.0423	-0.0435	-0.0489	-0.0525	-0.0545	-0.0554	-0.0557	0.0662	-0.0400
1H		0.0101	-0.0248	-0.0424	-0.0486	-0.0500	-0.0560	-0.0601	-0.0623	-0.0633	-0.0638	0.0739	-0.0461
range		0.091	0.099	0.102	0.103	0.104	0.108	0.111	0.113	0.114	0.114	max	0.0487
average		0.012	-0.005	-0.012	-0.015	-0.015	-0.018	-0.020	-0.020	-0.021	-0.021		
SD		0.026	0.033	0.039	0.041	0.041	0.043	0.045	0.045	0.046	0.046		
range	C2	0.050	0.077	0.091	0.097	0.098	0.103	0.107	0.109	0.110	0.110		
	C6	0.052	0.062	0.067	0.068	0.069	0.074	0.078	0.080	0.081	0.081	min	-0.0669
	C8	0.032	0.062	0.077	0.083	0.084	0.090	0.094	0.096	0.097	0.097	Δ	0.1156
average	C2	0.022	0.008	0.001	-0.002	-0.002	-0.004	-0.006	-0.006	-0.007	-0.007		
	C6	-0.012	-0.027	-0.034	-0.036	-0.036	-0.039	-0.040	-0.041	-0.041	-0.041		
	C8	0.025	0.005	-0.004	-0.007	-0.008	-0.011	-0.013	-0.014	-0.015	-0.015		

Table S3. The cSAR(NO₂) values for C2-, C6-, C8-NO₂ substituted purine tautomers, the nitro group 45° rotated, systems with I-type proximity in bold.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	average
9H	C2	-0.0196				-0.0713					-0.0834	0.0638	-0.0581
7H		-0.0204				-0.0766					-0.0904	0.0700	-0.0625
3H		0.0209				0.0129					0.0121	0.0088	0.0153
1H		0.0136				0.0062					0.0058	0.0077	0.0085
9H	C6	-0.0349				-0.0835					-0.0957	0.0608	-0.0714
7H		-0.0560				-0.0739					-0.0768	0.0208	-0.0689
3H		-0.0269				-0.0721					-0.0833	0.0564	-0.0608
1H		-0.0170				-0.0213					-0.0205	0.0043	-0.0196
9H	C8	0.0030				-0.0164					-0.0203	0.0233	-0.0113
7H		0.0157				-0.0017					-0.0055	0.0212	0.0028
3H		-0.0160				-0.0821					-0.0985	0.0825	-0.0655
1H		-0.0137				-0.0852					-0.1030	0.0893	-0.0673
range		0.077				0.098					0.115	max min Δ	0.0209 -0.1030 0.1240
average		-0.013				-0.047					-0.055		
SD		0.022				0.038					0.043		
range	C2	0.041				0.089					0.103		
	C6	0.039				0.062					0.075		
	C8	0.032				0.083					0.098		
average	C2	-0.001				-0.032					-0.039		
	C6	-0.034				-0.063					-0.069		
	C8	-0.003				-0.046					-0.057		

Table S4. HOMA values of five- and six-membered rings(5_{MR} , 6_{MR}), as well as calculated for all bonds (sum), and differences in HOMA between those obtained in formamide (FA) and gas phase (GP) for analyzed systems with in-plane, 45° and 90° rotated NO₂ group systems, with I-type proximity in bold.

GP				FA				
	6_{MR}	5_{MR}	sum	6_{MR}	5_{MR}	sum	FA-GP 6_{MR}	FA-GP 5_{MR}
9H	0.922	0.761	0.874	0.909	0.777	0.882	-0.014	0.016
7H	0.910	0.749	0.870	0.904	0.784	0.887	-0.006	0.036
3H	0.704	0.622	0.782	0.742	0.661	0.806	0.038	0.039
1H	0.600	0.530	0.730	0.697	0.624	0.786	0.097	0.093
9H	0.876	0.724	0.850	0.861	0.735	0.857	-0.015	0.010
7H	0.882	0.735	0.861	0.874	0.747	0.868	-0.008	0.013
3H	0.661	0.560	0.754	0.703	0.605	0.785	0.042	0.045
1H	0.425	0.313	0.629	0.547	0.438	0.700	0.122	0.125
9H	0.904	0.770	0.870	0.902	0.790	0.879	-0.002	0.019
7H	0.896	0.763	0.868	0.903	0.804	0.887	0.007	0.041
3H	0.782	0.730	0.835	0.833	0.780	0.869	0.051	0.050
1H	0.626	0.601	0.753	0.742	0.702	0.819	0.115	0.102
GP				FA				
45°	6_{MR}	5_{MR}	sum	6_{MR}	5_{MR}	sum	FA-GP 6_{MR}	FA-GP 5_{MR}
9H	0.923	0.759		0.910	0.773		-0.013	0.014
7H	0.910	0.754		0.905	0.790		-0.006	0.036
3H	0.710	0.628		0.749	0.669		0.040	0.041
1H	0.584	0.526		0.690	0.623		0.105	0.098
9H	0.907	0.752		0.893	0.763		-0.014	0.011
7H	0.897	0.748		0.888	0.765		-0.008	0.017
3H	0.723	0.629		0.760	0.666		0.038	0.037
1H	0.489	0.407		0.607	0.522		0.118	0.115
9H	0.914	0.764		0.913	0.784		-0.001	0.021
7H	0.907	0.750		0.913	0.796		0.006	0.046
3H	0.781	0.729		0.834	0.776		0.053	0.047
1H	0.628	0.598		0.745	0.698		0.117	0.099
GP				FA				
90°	6_{MR}	5_{MR}	sum	6_{MR}	5_{MR}	sum	FA-GP 6_{MR}	FA-GP 5_{MR}
9H	0.925	0.755		0.912	0.769		-0.013	0.014
7H	0.910	0.758		0.904	0.795		-0.007	0.037
3H	0.715	0.634		0.759	0.679		0.044	0.045
1H	0.563	0.515		0.683	0.623		0.120	0.107
9H	0.924	0.769		0.913	0.782		-0.011	0.013
7H	0.906	0.756		0.897	0.776		-0.010	0.020
3H	0.765	0.679		0.803	0.713		0.037	0.034
1H	0.551	0.503		0.663	0.601		0.112	0.098
9H	0.929	0.741		0.927	0.761		-0.001	0.020
7H	0.920	0.733		0.926	0.779		0.006	0.046
3H	0.780	0.728		0.836	0.772		0.056	0.044
1H	0.629	0.596		0.750	0.693		0.121	0.097

Table S5. Slopes, a , and determination coefficients, R^2 , linear relations of cSAR(NO₂) vs reciprocal of solvent permittivity, $1/\epsilon$, for C2-, C6-, and C8-NO₂ substituted 9H, 7H, 3H and 1H purine tautomers; systems with I-type proximity in bold.

	cSAR(NO ₂) vs $1/\epsilon$					
	coplanar with purine rings					
	C2		C6		C8	
	a	R^2	a	R^2	a	R^2
9H	0.0693	0.980	0.0672	0.973	0.0305	0.984
7H	0.0758	0.976	0.0250	0.994	0.0285	0.978
3H	0.0133	0.996	0.0624	0.975	0.0913	0.974
1H	0.0139	0.999	0.0105	0.995	0.0992	0.958
NO ₂	perpendicular to purine rings					
	C2		C6		C8	
	a	R^2	a	R^2	a	R^2
9H	0.0560	0.987	0.0540	0.981	0.0105	0.999
7H	0.0626	0.983	0.0163	0.996	0.0095	0.999
3H	0.0014	0.401	0.0505	0.981	0.0673	0.985
1H	-0.0012	0.200	-0.0044	0.597	0.0751	0.984

Table S6. The d_{NO} values (in Å) for C2-, C6-, C8 NO₂ substituted purine tautomers in the gas phase, tetrahydrofuran (THF) and formamide (FA) for in-plane, 45° and 90° rotated NO₂ group; systems with I-type proximity in bold.

in-plane		GP		THF		FA	
		$d_{\text{NO}\cdots(\text{H})}$	d_{NO}	$d_{\text{NO}\cdots(\text{H})}$	d_{NO}	$d_{\text{NO}\cdots(\text{H})}$	d_{NO}
9H	C2	1.2266	1.2284	1.2275	1.2302	1.2311	1.2306
7H		1.2279	1.2267	1.2273	1.2305	1.2302	1.2303
3H		1.2427	1.2205	1.2316	1.2400	1.2244	1.2322
1H		1.2461	1.2197	1.2329	1.2417	1.2247	1.2332
9H	C6	1.2255	1.2313	1.2284	1.2293	1.2332	1.2312
3H		1.2277	1.2294	1.2285	1.2303	1.2324	1.2313
7H		1.2447	1.2199	1.2323	1.2412	1.2250	1.2331
1H		1.2465	1.2234	1.2350	1.2423	1.2281	1.2352
9H	C8	1.2423	1.2244	1.2334	1.2403	1.2291	1.2347
7H		1.2426	1.2228	1.2327	1.2396	1.2279	1.2338
3H		1.2297	1.2315	1.2306	1.2338	1.2347	1.2342
1H		1.2306	1.2300	1.2303	1.2339	1.2338	1.2339
45°		GP		THF		FA	
9H	C2	1.2289	1.2278	1.2284	1.2308	1.2305	1.2307
7H		1.2286	1.2276	1.2281	1.2303	1.2309	1.2306
3H		1.2383	1.2232	1.2307	1.2358	1.2261	1.2310
1H		1.2411	1.2213	1.2312	1.2375	1.2250	1.2313
9H	C6	1.2308	1.2265	1.2286	1.2293	1.2322	1.2307
3H		1.2288	1.2280	1.2284	1.2311	1.2299	1.2305
7H		1.2401	1.2227	1.2314	1.2370	1.2265	1.2317
1H		1.2405	1.2236	1.2320	1.2368	1.2272	1.2320
9H	C8	1.2385	1.2259	1.2322	1.2365	1.2297	1.2331
7H		1.2391	1.2236	1.2314	1.2366	1.2277	1.2321
3H		1.2294	1.2310	1.2302	1.2333	1.2329	1.2331
1H		1.2299	1.2300	1.2300	1.2331	1.2327	1.2329
90°		GP		THF		FA	
9H	C2	1.2278	1.2278	1.2278	1.2293	1.2293	1.2293
7H		1.2278	1.2278	1.2278	1.2295	1.2295	1.2295
3H		1.2278	1.2277	1.2277	1.2274	1.2276	1.2275
1H		1.2280	1.2282	1.2281	1.2278	1.2277	1.2277
9H	C6	1.2274	1.2274	1.2274	1.2289	1.2289	1.2289
3H		1.2270	1.2270	1.2270	1.2285	1.2285	1.2285
7H		1.2291	1.2295	1.2293	1.2293	1.2292	1.2293
1H		1.2284	1.2283	1.2283	1.2282	1.2281	1.2281
9H	C8	1.2289	1.2288	1.2288	1.2289	1.2288	1.2288
7H		1.2288	1.2286	1.2287	1.2287	1.2287	1.2287
3H		1.2285	1.2285	1.2285	1.2301	1.2301	1.2301
1H		1.2285	1.2285	1.2285	1.2302	1.2302	1.2302

Table S7. Values of ONO angle for C2-, C6-, C8 NO₂ substituted purine tautomers in the gas phase (GP), tetrahydrofuran (THF) and formamide (FA) for in-plane, 45° and 90° rotated NO₂ group, systems with I-type proximity in bold.

in-plane		GP	<i>av</i>	THF	<i>av</i>	FA	<i>av</i>
C2	9H	126.38	<i>126.39</i>	125.18	<i>125.17</i>	124.89	<i>124.87</i>
	7H	126.40		125.16		124.84	
	3H	126.44	<i>126.36</i>	125.95	<i>125.90</i>	125.82	<i>125.78</i>
	1H	126.28		125.85		125.74	
C6	9H	126.62	<i>126.65</i>	125.46	<i>125.50</i>	125.16	<i>125.20</i>
	3H	126.68		125.53		125.24	
	7H	125.87	<i>126.07</i>	125.40	<i>125.61</i>	125.27	<i>125.48</i>
	1H	126.26		125.81		125.69	
C8	9H	126.65	<i>126.66</i>	126.01	<i>126.06</i>	125.85	<i>125.90</i>
	7H	126.68		126.10		125.95	
	3H	126.38	<i>126.35</i>	125.13	<i>125.11</i>	124.82	<i>124.80</i>
	1H	126.33		125.09		124.78	
45°		GP	<i>av</i>	THF	<i>av</i>	FA	<i>av</i>
C2	9H	126.81	<i>126.82</i>	125.83	<i>125.80</i>	125.60	<i>125.56</i>
	7H	126.83		125.77		125.52	
	3H	126.91	<i>126.92</i>	126.51	<i>126.51</i>	126.41	<i>126.41</i>
	1H	126.94		126.52		126.42	
C6	9H	127.03	<i>127.08</i>	126.08	<i>126.14</i>	125.83	<i>125.89</i>
	3H	127.12		126.20		125.95	
	7H	126.34	<i>126.63</i>	125.97	<i>126.24</i>	125.88	<i>126.14</i>
	1H	126.92		126.51		126.41	
C8	9H	126.89	<i>126.97</i>	126.36	<i>126.44</i>	126.23	<i>126.31</i>
	7H	127.06		126.53		126.39	
	3H	126.75	<i>126.75</i>	125.71	<i>125.69</i>	125.46	<i>125.44</i>
	1H	126.74		125.68		125.42	
90°		GP	<i>av</i>	THF	<i>av</i>	FA	<i>av</i>
C2	9H	127.09	<i>127.22</i>	126.27	<i>126.24</i>	126.10	<i>126.06</i>
	7H	127.36		126.21		126.02	
	3H	127.47	<i>127.42</i>	127.11	<i>127.08</i>	127.05	<i>127.01</i>
	1H	127.36		127.05		126.97	
C6	9H	127.33	<i>127.39</i>	126.54	<i>126.62</i>	126.35	<i>126.44</i>
	3H	127.46		126.70		126.52	
	7H	126.91	<i>127.16</i>	126.50	<i>126.81</i>	126.44	<i>126.75</i>
	1H	127.42		127.12		127.06	
C8	9H	127.29	<i>127.19</i>	126.89	<i>126.92</i>	126.79	<i>126.83</i>
	7H	127.08		126.96		126.87	
	3H	127.05	<i>127.05</i>	126.24	<i>126.22</i>	126.06	<i>126.03</i>
	1H	127.04		126.19		126.00	

Table S8. Distance (in Å) between O atom from NO₂ and N atom from the purine ring, O...N, in plane conformation (0°) for all cases substituted tautomers in the gas phase (GP), tetrahydrofuran (THF) and formamide (FA), systems with I-type proximity.

	GP		THF		FA		Δ	Δ
I type	O \cdots N _{7,3,1}	O \cdots N _{9,7,3}	O \cdots N _{7,3,1}	O \cdots N _{9,7,3}	O \cdots N _{7,3,1}	O \cdots N _{9,7,3}	Δ O \cdots N	Δ O \cdots N
C2	9H	2.654 2.636	2.653 2.639		2.652 2.640		0.002	0.005
	7H	2.644 2.643	2.648 2.644		2.648 2.644		0.004	0.001
C6	9H	2.662 2.925	2.661 2.928		2.662 2.926		0.001	0.002
	3H	2.638 2.943	2.640 2.941		2.641 2.940		0.003	0.003
C8	3H	2.725 2.717	2.724 2.721		2.724 2.722		0.001	0.005
	1H	2.713 2.726	2.717 2.727		2.718 2.727		0.005	0.001
Range Δ	0.307		0.302		0.299			
Δ C2	0.019		0.014		0.012			
Δ C6	0.305		0.301		0.299			
Δ C8	0.013		0.010		0.009			
average	2.719		2.720		2.720			
av C2	2.644		2.646		2.646			
av C6	2.792		2.792		2.792			
av C8	2.720		2.722		2.723			

O...N \rightarrow O...N_{7,3,1} O...N \rightarrow O...N_{9,7,3}

Table S9. Distance (in Å) between O atom from NO₂ and N atom from the purine ring, as O···N distance, and O···HN in plane conformation (0°) for all cases substituted tautomers in the gas phase (GP), tetrahydrofuran (THF) and formamide (FA), systems with II-type proximity.

		GP		THF		FA		Δ	Δ
II type		O···N	O···HN	O···N	O···HN	O···N	O···HN	O···N	O···NH
C2	3H	2.718	2.156	2.707	2.183	2.704	2.191	0.014	0.035
	1H	2.724	2.092	2.706	2.149	2.701	2.164	0.023	0.072
C6	7H	2.721	2.373	2.708	2.432	2.706	2.444	0.015	0.071
	1H	3.065	2.107	3.041	2.154	3.032	2.167	0.032	0.060
C8	9H	2.805	2.444	2.787	2.483	2.783	2.491	0.022	0.047
	7H	2.812	2.405	2.792	2.459	2.786	2.474	0.025	0.069
<i>range Δ</i>		0.346	0.352	0.335	0.334	0.331	0.327		
<i>Δ C2</i>		0.005	0.063	0.001	0.034	0.003	0.026		
<i>Δ C6</i>		0.344	0.265	0.333	0.278	0.326	0.276		
<i>Δ C8</i>		0.007	0.039	0.005	0.024	0.003	0.017		
<i>average</i>		2.673	2.765	2.674	2.766	2.674	2.767		
<i>av. C2</i>		2.721	2.124	2.707	2.166	2.703	2.177		
<i>av. C6</i>		2.893	2.240	2.874	2.293	2.869	2.305		
<i>av. C8</i>		2.808	2.425	2.790	2.471	2.785	2.483		

Table S10. Relative energies (in kcal/mol) of C2-, C6-, C8-NO₂ coplanar substituted purines.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	<i>average</i>
9H	C2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		3.33	2.00	1.07	0.70	0.61	0.21	-0.08	-0.24	-0.31	-0.34	3.67	0.70
3H		8.17	9.87	10.68	11.79	11.02	11.29	11.47	11.56	11.60	11.62	3.62	10.91
1H		9.69	9.95	9.82	9.72	9.70	9.57	9.46	9.39	9.36	9.35	0.60	9.60
9H	C6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		-4.06	-3.02	-2.57	-2.42	-2.39	-2.26	-2.18	-2.14	-2.12	-2.11	1.95	-2.53
3H		10.16	9.22	8.68	8.48	8.44	8.23	8.10	8.02	7.99	7.97	2.19	8.53
1H		10.34	10.40	10.24	10.14	10.11	9.99	9.89	9.83	9.81	9.80	0.61	10.06
9H	C8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		3.67	2.73	2.01	1.71	1.65	1.32	1.09	0.96	0.90	0.87	2.81	1.69
3H		8.96	5.82	4.16	3.56	3.42	2.83	2.42	2.20	2.10	2.06	6.90	3.75
1H		11.55	6.40	3.62	2.55	2.32	1.24	0.50	0.10	-0.08	-0.16	11.71	2.80
<i>range</i>		15.61	13.42	13.25	14.21	13.41	13.55	13.65	13.7	13.72	13.73		
<i>average</i>		5.15	4.45	3.98	3.85	3.74	3.54	3.39	3.31	3.27	3.26		
<i>SD</i>		5.28	4.74	4.70	4.85	4.74	4.80	4.85	4.88	4.90	4.90		
<i>range</i>	C2	9.69	9.95	10.68	11.79	11.02	11.29	11.55	11.80	11.91	11.96		
	C6	14.40	13.43	12.81	12.56	12.51	12.25	12.07	11.97	11.92	11.90		
	C8	11.55	6.40	4.16	3.56	3.42	2.83	2.42	2.20	2.18	2.22		
<i>average</i>	C2	5.30	5.45	5.39	5.55	5.33	5.27	5.21	5.18	5.16	5.16		
	C6	4.11	4.15	4.09	4.05	4.04	3.99	3.95	3.93	3.92	3.92		
	C8	6.05	3.74	2.45	1.96	1.85	1.35	1.00	0.82	0.73	0.69		

Table S11. Relative energies (in kcal/mol) of C2-, C6-, C8-NO₂ perpendicular (90°) substituted purines.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	<i>average</i>
9H	C2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		2.97	1.67	0.80	0.45	0.37	0.01	-0.26	-0.40	-0.47	-0.50	3.47	0.47
3H		15.29	15.73	15.85	15.88	15.88	15.88	15.87	15.86	15.86	15.85	0.59	15.79
1H		17.83	16.57	15.63	15.23	15.14	14.70	14.38	14.20	14.12	14.08	3.75	15.19
9H	C6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		2.84	2.47	2.13	1.98	1.94	1.76	1.62	1.54	1.50	1.49	1.36	1.93
3H		9.79	8.90	8.39	8.19	8.15	7.95	7.81	7.74	7.70	7.69	2.10	8.23
1H		18.26	16.85	15.86	15.45	15.35	14.90	14.57	14.38	14.29	14.25	4.01	15.42
9H	C8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		3.30	2.23	1.48	1.17	1.10	0.76	0.52	0.38	0.32	0.29	3.01	1.16
3H		2.87	1.10	0.21	-0.10	-0.17	-0.47	-0.67	-0.77	-0.82	-0.84	3.71	0.04
1H		4.82	1.19	-0.83	-1.57	-1.73	-2.47	-2.98	-3.25	-3.38	-3.43	8.25	-1.36
<i>range</i>		18.26	16.85	16.69	17.45	17.61	18.35	18.85	19.11	19.24	19.28		
<i>average</i>		6.50	5.56	4.96	4.72	4.67	4.42	4.24	4.14	4.09	4.07		
<i>SD</i>		6.96	6.95	6.94	6.94	6.94	6.94	6.93	6.93	6.93	6.93		
<i>range</i>	C2	17.83	16.57	15.85	15.88	15.88	15.88	16.13	16.26	16.32	16.35		
	C6	18.26	16.85	15.86	15.45	15.35	14.90	14.57	14.38	14.29	14.25		
	C8	4.82	2.23	2.30	2.74	2.83	3.23	3.50	3.64	3.70	3.73		
<i>average</i>	C2	9.02	8.49	8.07	7.89	7.85	7.65	7.50	7.42	7.38	7.36		
	C6	7.72	7.06	6.59	6.40	6.36	6.15	6.00	5.91	5.87	5.86		
	C8	2.75	1.13	0.22	-0.13	-0.20	-0.54	-0.78	-0.91	-0.97	-1.00		

Table S12. Dipole moments, μ , (in D) of C2-, C6-, C8-NO₂ coplanar substituted purines; systems with I-type proximity in bold.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	average
9H	C2	7.02	8.21	8.85	9.09	9.14	9.37	9.53	9.62	9.66	9.68	2.66	9.02
7H		9.97	11.63	12.55	12.89	12.97	13.31	13.55	13.68	13.74	13.77	3.79	12.81
3H		1.17	1.26	1.32	1.34	1.35	1.38	1.40	1.42	1.42	1.42	0.25	1.35
1H		4.78	5.76	6.38	6.62	6.67	6.93	7.10	7.20	7.25	7.27	2.49	6.60
9H	C6	7.28	8.51	9.19	9.44	9.50	9.75	9.93	10.02	10.07	10.09	2.80	9.38
7H		3.54	4.27	4.70	4.87	4.91	5.08	5.20	5.27	5.30	5.31	1.77	4.84
3H		6.98	8.19	8.87	9.12	9.18	9.44	9.61	9.71	9.76	9.77	2.79	9.06
1H		4.14	5.14	5.75	6.00	6.05	6.30	6.48	6.58	6.62	6.64	2.50	5.97
9H	C8	2.45	2.85	3.07	3.16	3.18	3.27	3.33	3.37	3.38	3.39	0.94	3.14
7H		4.52	5.38	5.92	6.13	6.18	6.40	6.56	6.65	6.69	6.71	2.19	6.12
3H		8.12	9.64	10.47	10.77	10.84	11.15	11.36	11.47	11.52	11.54	3.42	10.69
1H		11.42	13.43	14.75	15.19	15.29	15.73	16.04	16.20	16.28	16.31	4.89	15.06
range		10.25	12.17	13.44	13.85	13.94	14.35	14.63	14.79	14.86	14.89		
average		5.95	7.02	7.65	7.89	7.94	8.18	8.34	8.43	8.47	8.49		
SD		2.92	3.42	3.72	3.82	3.84	3.94	4.00	4.04	4.06	4.06		

Table S13. Dipole moments, μ , (in D) of C2-, C6-, C8-NO₂ perpendicular (90°) substituted purines; systems with I-type proximity in bold.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	Δ	average
9H	C2	6,45	7,48	8,01	8,20	8,24	8,43	8,55	8,62	8,65	8,67	2,22	8,13
7H		9,44	10,95	11,76	12,06	12,12	12,42	12,62	12,74	12,79	12,81	3,37	11,97
3H		1,00	1,20	1,37	1,44	1,46	1,54	1,60	1,63	1,64	1,65	0,65	1,45
1H		5,25	6,31	6,95	7,21	7,26	7,53	7,72	7,82	7,87	7,89	2,64	7,18
9H	C6	6,69	7,75	8,32	8,53	8,57	8,78	8,92	9,00	9,03	9,05	2,36	8,46
7H		3,88	4,64	5,08	5,25	5,29	5,46	5,59	5,66	5,69	5,71	1,83	5,23
3H		6,50	7,61	8,22	8,45	8,50	8,72	8,88	8,97	9,01	9,03	2,52	8,39
1H		5,08	6,18	6,85	7,11	7,17	7,44	7,64	7,74	7,80	7,82	2,74	7,08
9H	C8	2,08	2,38	2,57	2,65	2,66	2,75	2,81	2,84	2,86	2,87	0,78	2,65
7H		4,62	5,43	5,94	6,14	6,19	6,40	6,55	6,64	6,68	6,69	2,07	6,13
3H		7,22	8,51	9,17	9,41	9,46	9,70	9,86	9,94	9,98	10,00	2,78	9,32
1H		10,57	12,50	13,53	13,90	13,98	14,35	14,60	14,74	14,80	14,83	4,26	13,78
range		9,56	11,31	12,16	12,46	12,53	12,81	13,01	13,11	13,16	13,18		
average		5,73	6,74	7,31	7,53	7,57	7,79	7,95	8,03	8,07	8,08		
SD		2,62	3,07	3,28	3,36	3,37	3,45	3,49	3,52	3,53	3,54		

Table S14. Solvation energies (in kcal/mol) of C2-, C6-, C8-NO₂ coplanar substituted purines.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	average
9H	C2	0.00	-5.79	-8.85	-9.96	-10.20	-11.30	-12.04	-12.44	-12.63	-12.71	-9.59
7H		0.00	-7.12	-11.11	-12.60	-12.92	-14.42	-15.45	-16.01	-16.27	-16.38	-12.23
3H		0.00	-4.09	-6.34	-6.34	-7.35	-8.17	-8.74	-9.05	-9.19	-9.25	-6.85
1H		0.00	-5.53	-8.72	-9.93	-10.19	-11.42	-12.27	-12.74	-12.96	-13.05	-9.68
9H	C6	0.00	-5.58	-8.62	-9.74	-9.99	-11.11	-11.88	-12.29	-12.48	-12.57	-9.43
7H		0.00	-4.54	-7.13	-8.11	-8.32	-9.31	-10.00	-10.37	-10.54	-10.61	-7.89
3H		0.00	-6.52	-10.10	-11.43	-11.71	-13.03	-13.94	-14.43	-14.66	-14.75	-11.06
1H		0.00	-5.51	-8.72	-9.94	-10.21	-11.46	-12.32	-12.80	-13.02	-13.11	-9.71
9H	C8	0.00	-3.68	-5.68	-6.42	-6.58	-7.31	-7.82	-8.09	-8.22	-8.27	-6.21
7H		0.00	-4.63	-7.34	-8.38	-8.61	-9.67	-10.41	-10.81	-11.00	-11.07	-8.19
3H		0.00	-6.81	-10.48	-11.82	-12.11	-13.44	-14.36	-14.85	-15.08	-15.17	-11.41
1H		0.00	-8.83	-13.61	-15.41	-15.81	-17.62	-18.86	-19.53	-19.85	-19.98	-14.95
range			5.15	7.93	9.07	9.23	10.31	11.04	11.44	11.63	11.71	
average			-5.72	-8.89	-10.01	-10.33	-11.52	-12.34	-12.78	-12.99	-13.08	
SD			1.44	2.21	2.59	2.56	2.85	3.04	3.15	3.20	3.22	
range	C2		3.03	4.77	6.26	5.58	6.24	6.71	6.96	7.08	7.13	
	C6		1.98	2.97	3.32	3.39	3.73	3.95	4.06	4.12	4.14	
	C8		5.15	7.93	9.00	9.23	10.30	11.04	11.44	11.63	11.71	
average	C2		-5.63	-8.75	-9.70	-10.16	-11.33	-12.13	-12.56	-12.76	-12.85	
	C6		-5.54	-8.64	-9.80	-10.06	-11.23	-12.04	-12.47	-12.67	-12.76	
	C8		-5.99	-9.28	-10.51	-10.78	-12.01	-12.86	-13.32	-13.53	-13.62	

Table S15. Solvation energies (in kcal/mol) of C2-, C6-, C8-NO₂ perpendicular (90°) substituted purines.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	average
9H	C2	0.00	-4.85	-7.33	-8.22	-8.41	-9.27	-9.86	-10.18	-10.32	-10.38	-7.88
7H		0.00	-6.14	-9.50	-10.73	-11.00	-12.24	-13.09	-13.55	-13.76	-13.85	-10.39
3H		0.00	-4.41	-6.77	-7.63	-7.82	-8.69	-9.29	-9.61	-9.76	-9.82	-7.38
1H		0.00	-6.11	-9.54	-10.82	-11.10	-12.41	-13.31	-13.81	-14.04	-14.13	-10.53
9H	C6	0.00	-4.66	-7.09	-7.97	-8.16	-9.03	-9.62	-9.94	-10.09	-10.15	-7.67
7H		0.00	-5.03	-7.81	-8.84	-9.07	-10.12	-10.85	-11.24	-11.43	-11.51	-8.59
3H		0.00	-5.55	-8.50	-9.57	-9.80	-10.87	-11.60	-11.99	-12.17	-12.25	-9.23
1H		0.00	-6.07	-9.49	-10.79	-11.07	-12.39	-13.32	-13.82	-14.06	-14.16	-10.52
9H	C8	0.00	-3.83	-5.87	-6.61	-6.78	-7.52	-8.03	-8.30	-8.43	-8.49	-6.39
7H		0.00	-4.91	-7.70	-8.75	-8.98	-10.06	-10.81	-11.22	-11.42	-11.50	-8.54
3H		0.00	-5.61	-8.53	-9.59	-9.82	-10.86	-11.57	-11.95	-12.12	-12.20	-9.23
1H		0.00	-7.46	-11.51	-13.00	-13.32	-14.81	-15.83	-16.37	-16.63	-16.74	-12.57
range			3.63	5.64	6.39	6.54	7.29	7.8	8.07	8.2	8.25	
average			-5.39	-8.30	-9.38	-9.61	-10.69	-11.43	-11.83	-12.02	-12.10	
SD			0.98	1.54	1.75	1.80	2.02	2.17	2.25	2.29	2.31	
range	C2		1.73	2.77	3.19	3.28	3.72	4.03	4.20	4.28	4.31	
	C6		1.41	2.40	2.82	2.91	3.36	3.69	3.88	3.97	4.01	
	C8		3.63	5.64	6.39	6.55	7.29	7.80	8.07	8.20	8.25	
average	C2		-5.38	-8.28	-9.35	-9.58	-10.65	-11.39	-11.79	-11.97	-12.05	
	C6		-5.32	-8.22	-9.29	-9.53	-10.60	-11.35	-11.75	-11.94	-12.02	
	C8		-5.45	-8.40	-9.49	-9.73	-10.81	-11.56	-11.96	-12.15	-12.23	

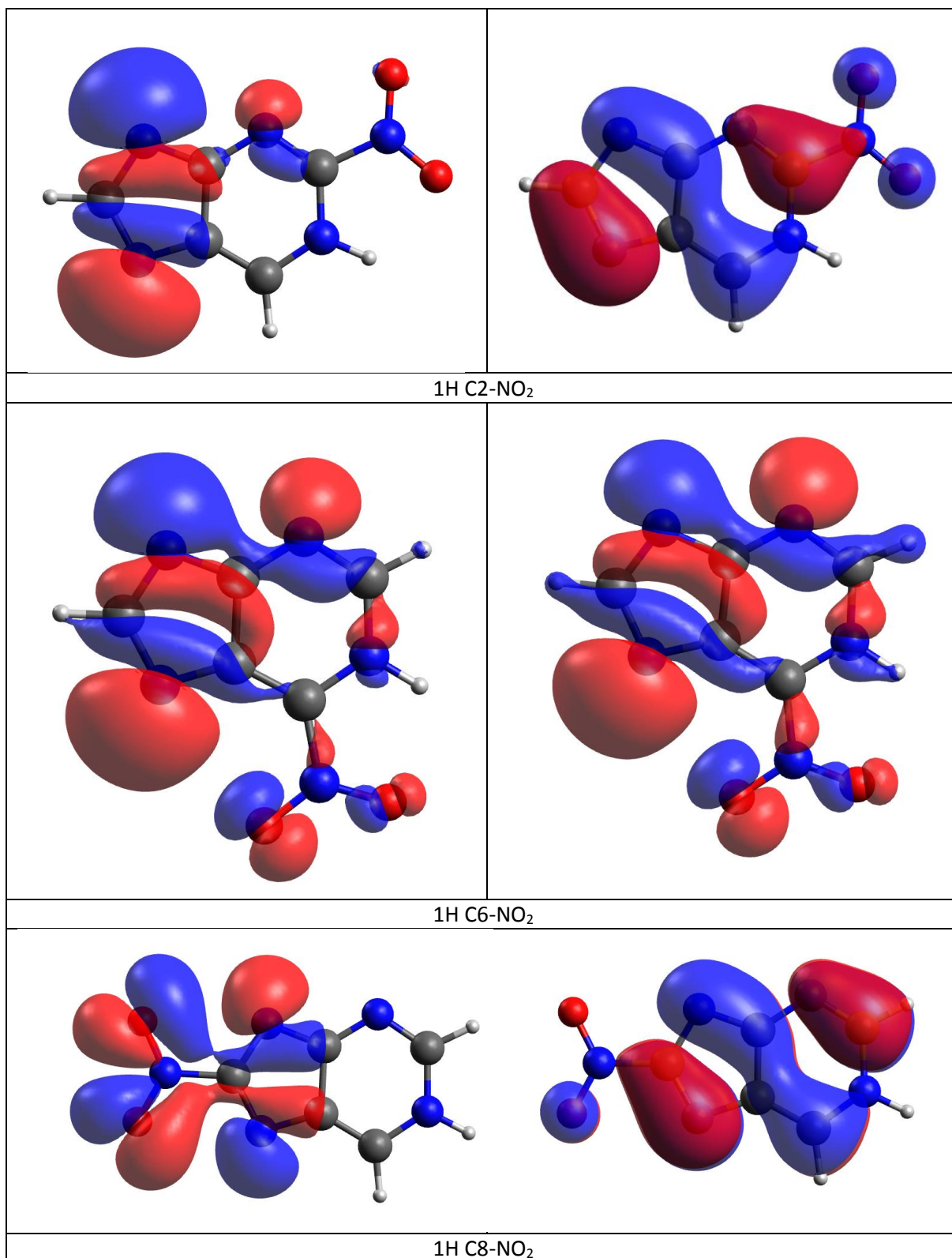
Table S16. Solvation Gibbs free energies (in kcal/mol) of C2-, C6-, C8-NO₂ coplanar substituted purines.

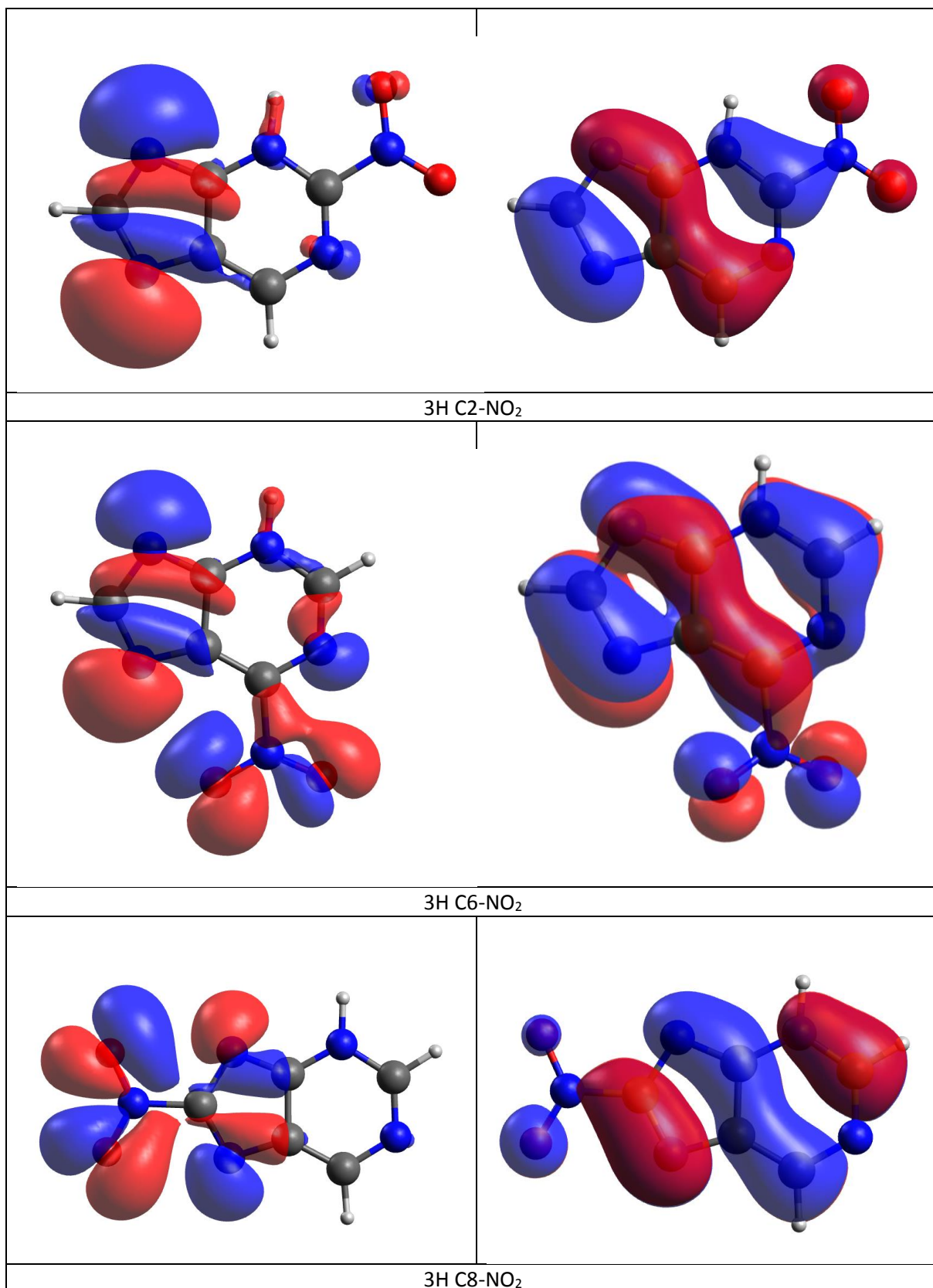
		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	<i>average</i>
9H	C2	0.00	-5.64	-8.65	-9.74	-9.98	-11.52	-12.27	-12.21	-12.40	-12.47	-10.54
7H		0.00	-6.88	-10.77	-12.23	-12.55	-14.02	-15.04	-15.60	-15.86	-15.96	-13.21
3H		0.00	-4.09	-6.34	-7.17	-7.35	-8.18	-8.76	-9.07	-9.22	-9.28	-7.72
1H		0.00	-5.50	-8.63	-9.81	-10.07	-11.27	-12.11	-12.56	-12.77	-12.85	-10.62
9H	C6	0.00	-5.44	-8.43	-9.53	-9.77	-10.87	-11.63	-12.04	-12.23	-12.31	-10.25
7H		0.00	-4.54	-7.09	-8.04	-8.25	-9.21	-9.88	-10.23	-10.40	-10.47	-8.68
3H		0.00	-6.44	-9.97	-11.27	-11.55	-12.85	-13.74	-14.22	-14.44	-14.53	-12.11
1H		0.00	-5.39	-8.57	-9.78	-10.05	-11.28	-12.15	-12.62	-12.84	-12.93	-10.62
9H	C8	0.00	-3.67	-5.65	-6.38	-6.54	-7.28	-7.79	-8.07	-8.20	-8.25	-6.87
7H		0.00	-4.48	-7.13	-8.16	-8.39	-9.45	-10.20	-10.61	-10.80	-10.88	-8.90
3H		0.00	-6.83	-10.50	-11.80	-12.09	-13.42	-14.34	-14.83	-15.06	-15.14	-12.67
1H		0.00	-9.07	-13.29	-15.03	-15.41	-17.14	-19.34	-20.01	-20.33	-20.47	-16.68
<i>range</i>			5.40	7.64	8.65	8.87	9.86	11.55	11.95	12.14	12.22	
<i>average</i>			-5.66	-8.75	-9.91	-10.17	-11.37	-12.27	-12.67	-12.88	-12.96	
<i>SD</i>			1.42	2.05	2.30	2.36	2.62	2.99	3.09	3.14	3.16	
<i>range</i>	C2		2.79	4.43	5.06	5.20	5.84	6.28	6.52	6.64	6.68	
	C6		1.90	2.88	3.23	3.30	3.64	3.87	3.98	4.04	4.06	
	C8		5.40	7.64	8.65	8.87	9.86	11.55	11.95	12.14	12.22	
<i>average</i>	C2		-5.53	-8.60	-9.74	-9.99	-11.25	-12.05	-12.36	-12.56	-12.64	
	C6		-5.45	-8.52	-9.66	-9.91	-11.05	-11.85	-12.28	-12.48	-12.56	
	C8		-6.01	-9.14	-10.34	-10.61	-11.82	-12.92	-13.38	-13.60	-13.68	

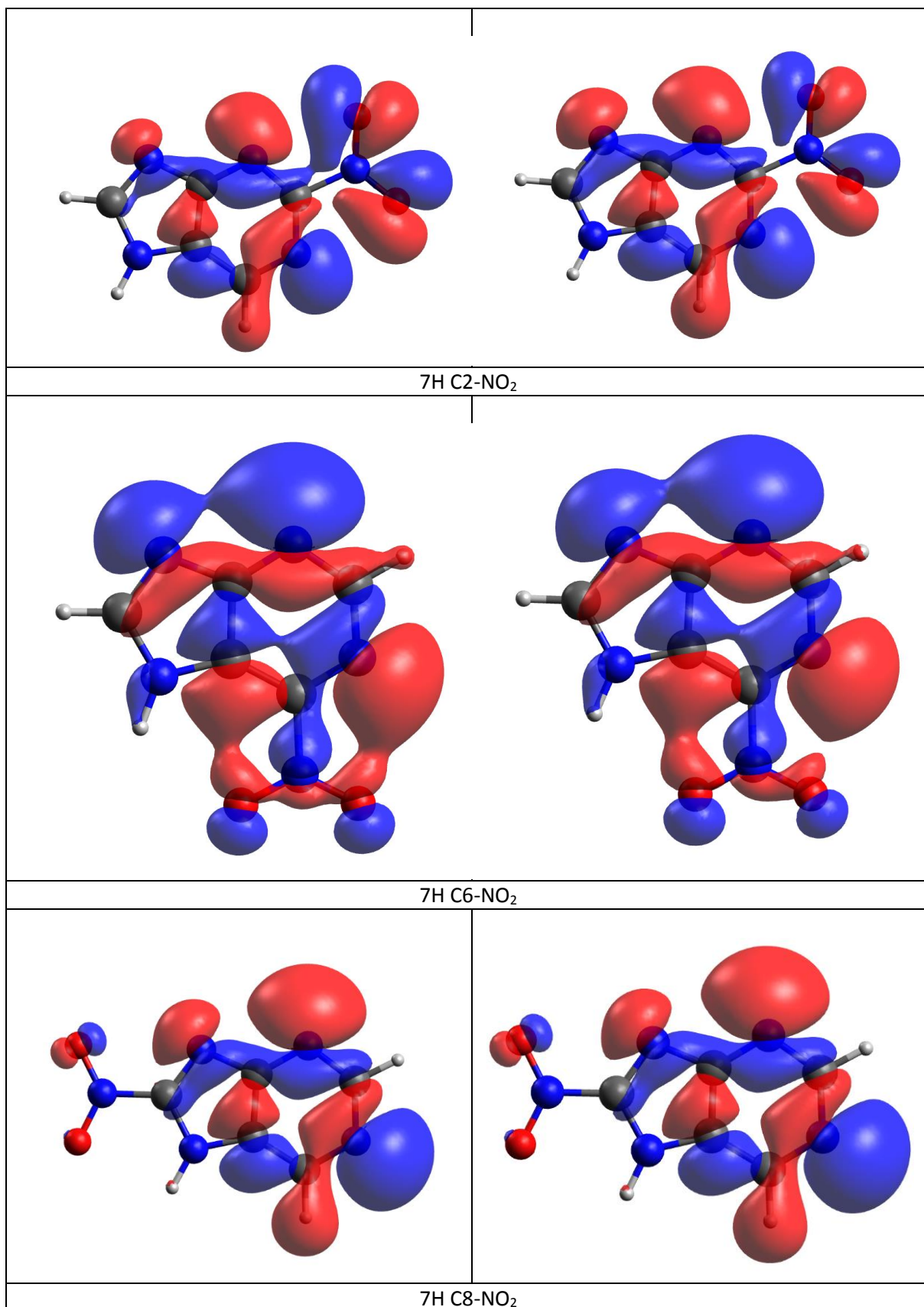
Table S17. Relative Gibbs free energies (in kcal/mol) of C2-, C6-, C8-NO₂ coplanar substituted purines.

		GP	Tol	ClF	o-Cr	THF	Py	EtOH	DMSO	H ₂ O	FA	<i>range</i>
9H	C2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		3.19	1.94	1.06	0.70	0.62	0.68	0.41	-0.20	-0.27	-0.30	3.49
3H		7.44	8.98	9.75	10.02	10.07	10.78	10.95	10.58	10.62	10.64	3.51
1H		9.03	9.16	9.04	8.95	8.93	9.27	9.19	8.68	8.66	8.65	0.63
9H	C6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		-4.61	-3.70	-3.27	-3.12	-3.09	-2.95	-2.85	-2.80	-2.78	-2.78	1.83
3H		10.13	9.14	8.59	8.39	8.35	8.15	8.02	7.95	7.92	7.90	2.23
1H		9.50	9.54	9.35	9.25	9.22	9.09	8.98	8.92	8.89	8.87	0.67
9H	C8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7H		3.52	2.71	2.03	1.74	1.67	1.35	1.11	0.98	0.92	0.89	2.63
3H		9.69	6.52	4.84	4.26	4.13	3.54	3.13	2.92	2.82	2.80	6.89
1H		12.26	6.85	4.61	3.61	3.39	2.40	0.70	0.31	0.12	0.04	12.22
<i>range</i>		16.87	13.25	13.02	13.14	13.16	13.72	13.80	13.38	13.40	13.41	
<i>average</i>		5.01	4.26	3.83	3.65	3.61	3.53	3.30	3.11	3.07	3.06	
<i>SD</i>		5.13	4.43	4.30	4.29	4.29	4.39	4.46	4.39	4.40	4.41	
<i>range</i>	C2	9.03	9.16	9.75	10.02	10.07	10.78	10.95	10.78	10.89	10.94	
	C6	14.74	13.25	12.62	12.36	12.31	12.03	11.83	11.72	11.67	11.65	
	C8	12.26	6.85	4.84	4.26	4.13	3.54	3.13	2.92	2.82	2.80	
<i>average</i>	C2	4.91	5.02	4.96	4.92	4.91	5.18	5.14	4.76	4.75	4.74	
	C6	3.75	3.74	3.67	3.63	3.62	3.57	3.54	3.52	3.51	3.50	
	C8	6.37	4.02	2.87	2.40	2.30	1.82	1.24	1.05	0.96	0.93	

Figure S1. Representations of HOMO orbitals of NO₂ substituted adenine tautomers in the gas phase and formamide solution (0.02 isosurface). Left column: gas phase, right column: formamide.







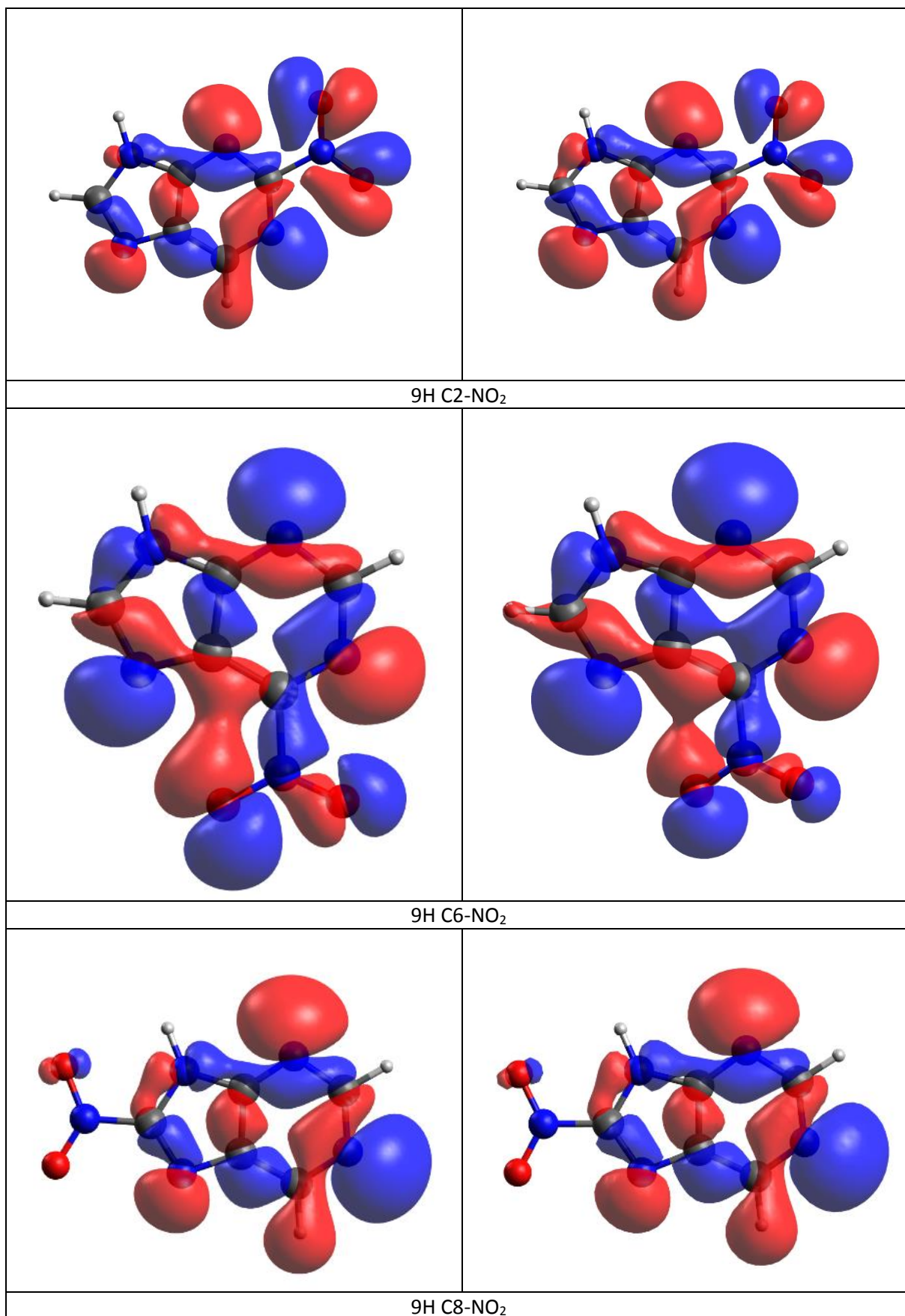


Figure S2. Representations of LUMO orbitals of NO₂ substituted adenine tautomers in the gas phase and in formamide solution (0.02 isosurface). Left column: gas phase, right column: formamide.

