SUPPORTING INFORMATION

Effect of substituents on the excited-state dynamics of the modified DNA bases 2,4-diaminopyrimidine and 2,6-diaminopurine

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Figure S1. Photoelectron spectrum and calculated ionization potentials for all the possible tautomers of 2,4-diaminopyrimidine. The ionization potentials were calculated at the ROVGF/6-311+G(2d,p) level and clearly show that only the diamino form were observed in the experiment.

Table S1 Assignment of the photoelectron spectrum of 2,4-diaminopyrimidine

2,4-diaminopyrimidine						
Transition		Exp.	(TD)-B3LYP 6-311+G(2d,p)	electronic configuration	ROVGF 6-311+G(2d,p)	electronic configuration
$S_1 \leftarrow S_0$		4.28	4.81	$\pi^{*1}\pi^1 n^2\pi^2 n^2\pi^2\pi^2$		
$D_0 \leftarrow S_0$	IE_{ad}	7.81	7.86	$\pi^{*0}\pi^1\pi^2 n^2 n^2\pi^2\pi^2$		
	IE_{vert}	8.30	8.13		8.1	$\pi^{*0}\pi^1\pi^2 n^2\pi^2 n^2\pi^2$
$D_1 \leftarrow S_0$		1.34	1.1	$\pi^{*0}\pi^2\pi^2 n^1 n^2\pi^2\pi^2$		
	IE_{vert}	9.15			9.38	$\pi^{*0}\pi^2\pi^1 n^2\pi^2 n^2\pi^2$
$D_2 \leftarrow S_0$		1.69	1.49	$\pi^{*0}\pi^2\pi^1 n^2 n^2\pi^2\pi^2$		
	IE_{vert}	9.50			9.39	$\pi^{*0}\pi^2\pi^2 n^1\pi^2 n^2\pi^2$
$D_3 \leftarrow S_0$		2.91	2.73	$\pi^{*0}\pi^2\pi^2 n^2 n^1\pi^2\pi^2$		
	IE_{vert}	10.72			11.00	$\pi^{*0}\pi^2\pi^2 n^2\pi^1 n^2\pi^2$
$D_4 \leftarrow S_0$		3.25	3.1	$\pi^{*0}\pi^2\pi^2 n^2 n^2\pi^1\pi^2$		
	IE_{vert}	11.06			11.18	$\pi^{*0}\pi^2\pi^2 n^2\pi^2 n^1\pi^2$
$D_5 \leftarrow S_0$		4.31	4.31	$\pi^{*0}\pi^2\pi^2 n^2 n^2\pi^2\pi^1$		
	IE_{vert}	12.22			12.62	$\pi^{*0}\pi^2\pi^2 n^2\pi^2 n^2\pi^1$
Onset		5.70	4.79			
	IE_{onset}	13.51			13.93	

7H-2,6-diaminopurine				
Transition	Exp.	(TD)-B3LYP 6-311+G(2d,p)	electronic configuration	osc. strength
$S_1 \leftarrow S_0$	3.99	4.28	$\pi^{*1}\pi^1 n^2\pi^2\pi^2$	0.10
9H-2,6-diaminopurine				
$S_1 \leftarrow S_0$	4.33	4.66	$\pi^{*1}\pi^1 n^2\pi^2\pi^2$	0.17

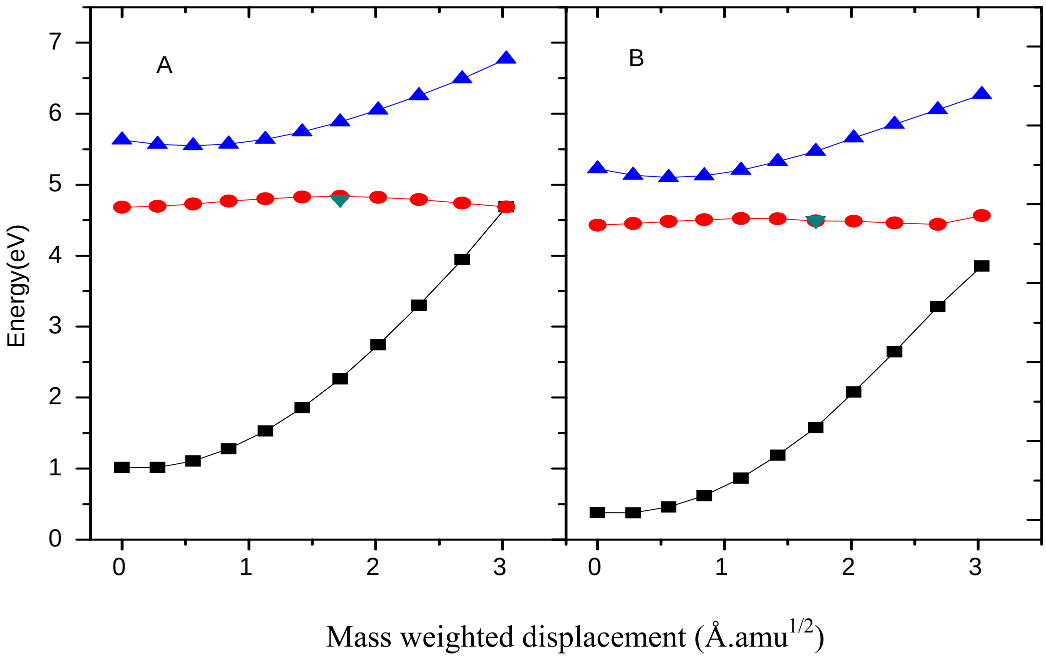
Table S2.. Vertical excitation energies calculated at the RICC2 level with various basis sets.

	SVP[1,2]	TZVP[3]	TZVPP	aug-TZVP	aug-TZVPP
$2^1A(\pi\pi^*)$	5.10	4.98	4.94	4.85[a]	4.86[a]
$3^1A(n\pi^*)$	5.16	5.11	5.02	4.96[a]	4.95[a]
$4^1A(n\pi^*)$	5.88	5.79[a]	5.72[a]	5.36 (π ->Ryd)	5.44 (π ->Ryd)
$5^1A(\pi\pi^*)$	6.31	6.06	6.01[a]	5.60 (n -> Ryd)	5.60 (n -> Ryd)

[a]the state has partially Rydberg character

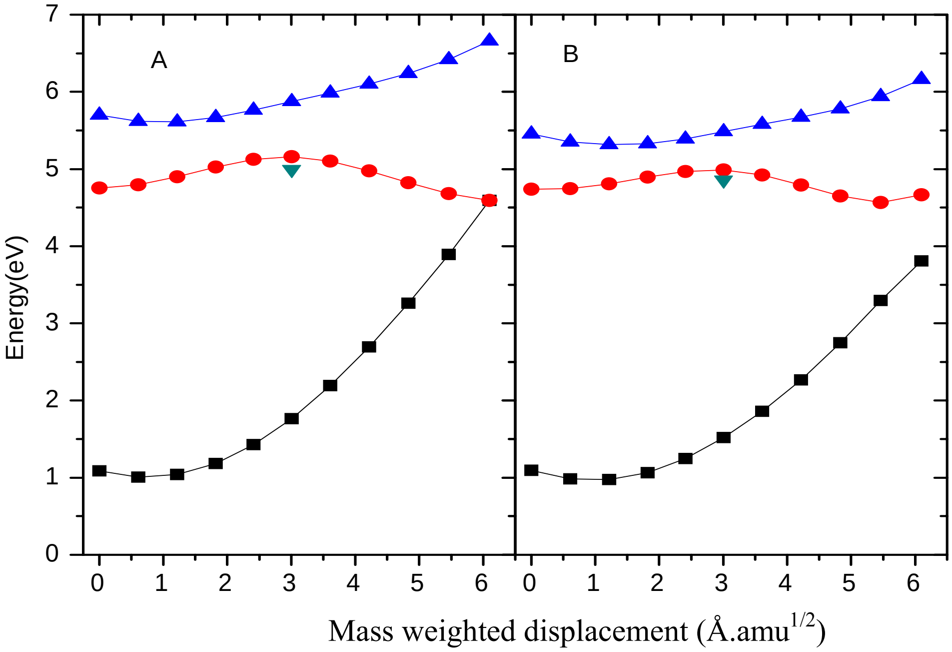
Figure S2. The interpolation curves between the S1min_C2 and S1min_C6 minima towards various MXS structures calculated at the CASSCF and MR-CISD(17)+Q

S1min_C6 to $^{1}S_{6}$

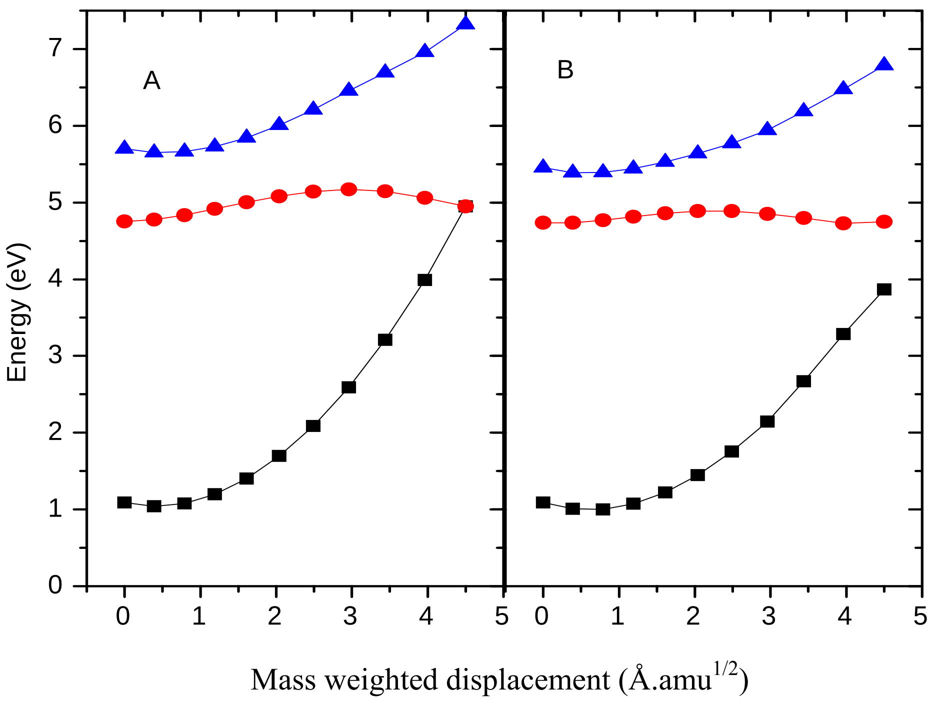


A-CASSCF(14,10) , B-MR-CISD(17)+Q
Green point indicates the saddle point

S1min_C6 to $^3H_4$



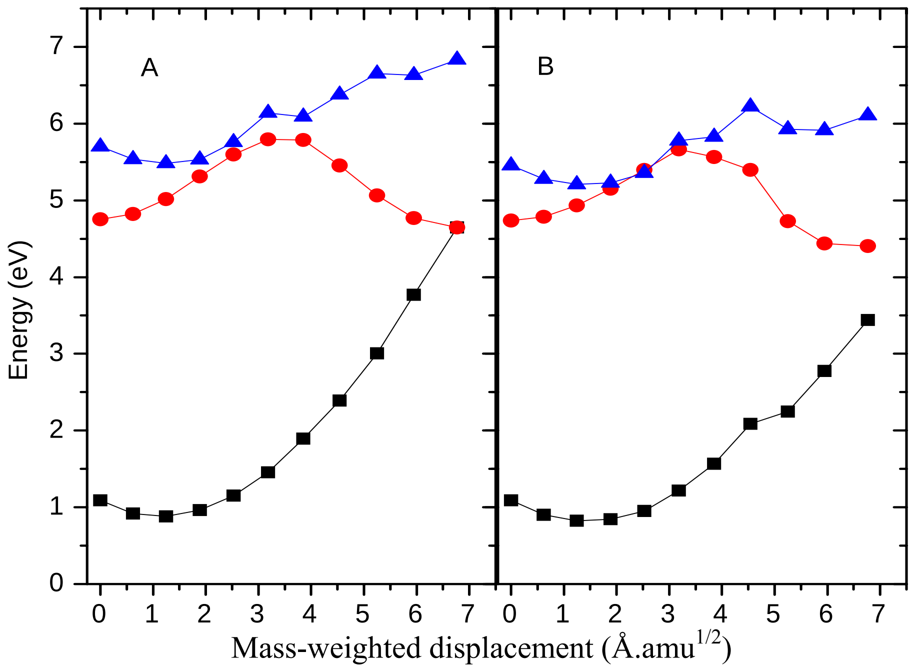
S1min_6 to $B_{1,4}$



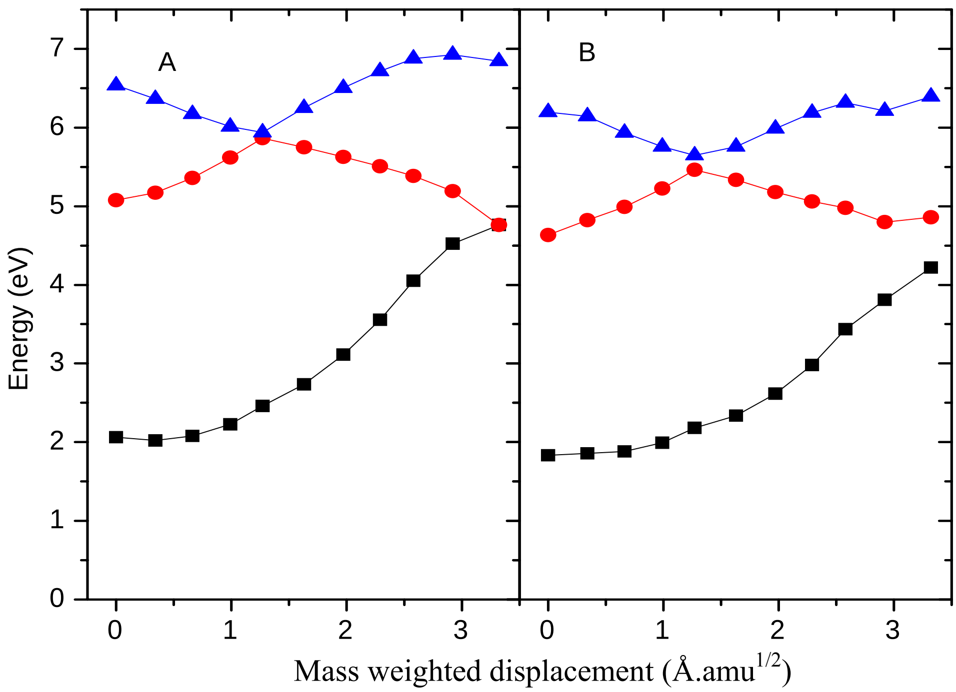
A-CASSCF(14,10) , B-MR-CISD(17)+Q

Green point indicates the saddle point

S1min_6 to $^1S_2$

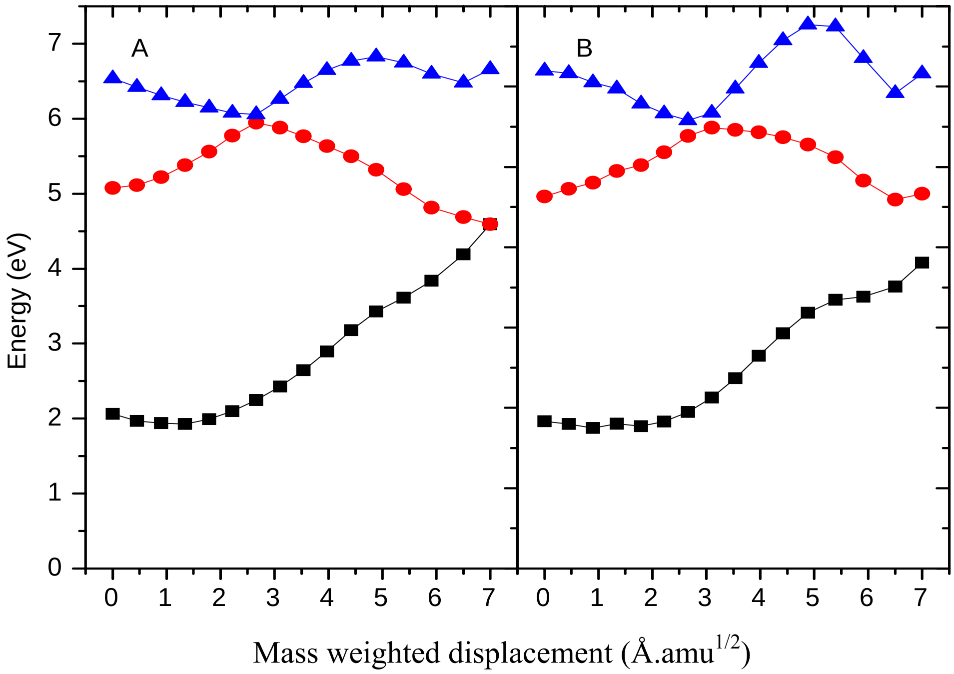


S1min_2 to $^1S_6$

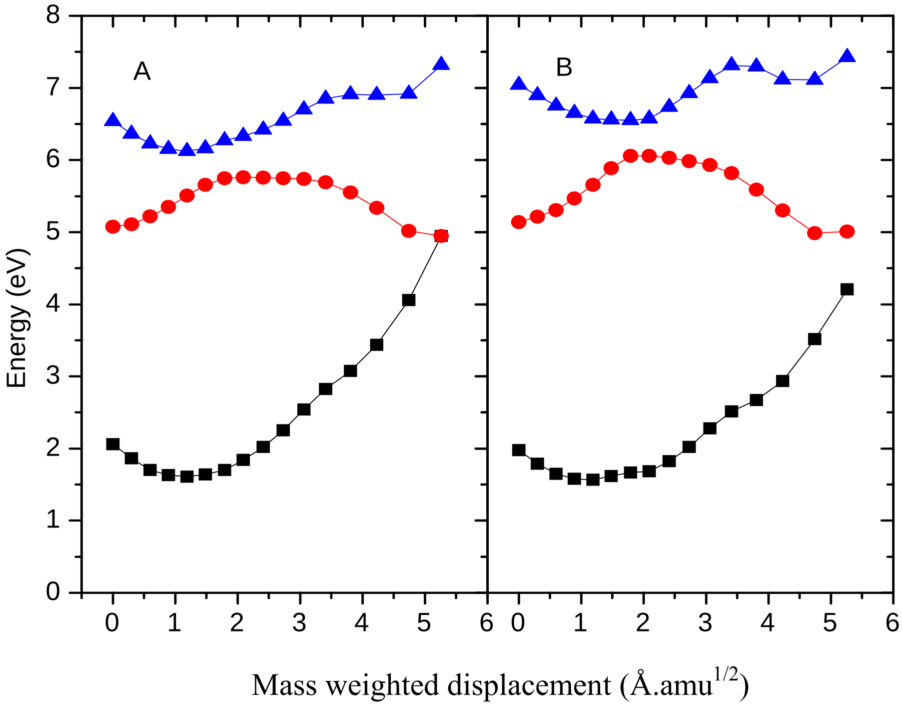


A-CASSCF(14,10) , B-MR-CISD(17)+Q

S1min_2 to $^3H_4$

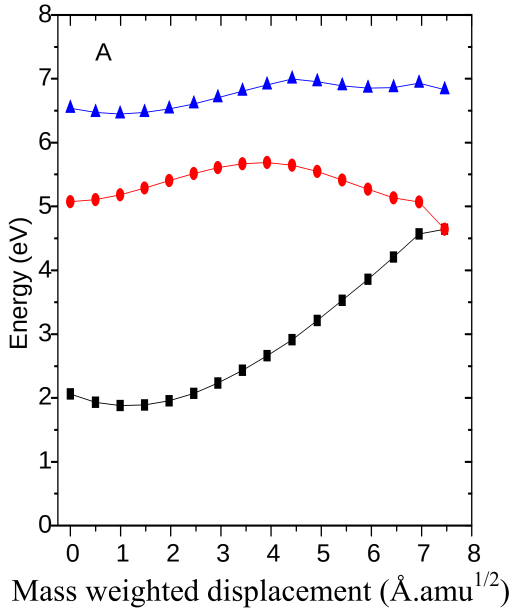


S1min_2 to $B_{1,4}$



A-CASSCF(14,10) , B-MR-CISD(17)+Q

S1min_2 to $^1S_2$



A-CASSCF(14,10) , B-MR-CISD(17)+Q

Due to a mixed character of the CI wavefunction in the MR-CISD(17)+Q calculations of LIIC from S1min_C2 towards $^1S_2$ are not reported.

XYZ coordinates of MXS(S_1/S_0) structures optimized at the CASSCF(14,10)/6-31G level**

MXS_$^1S_2$

N	-1.493227	3.066299	0.050894
N	-0.318478	1.063764	0.383469
N	-0.271445	5.031078	0.137813
N	-1.261036	1.524851	-1.755511
C	-0.356000	3.660768	-0.002369
C	0.930340	2.922565	-0.174381
C	0.907386	1.560345	0.043697
C	-1.297581	1.706812	-0.355185
H	1.852402	3.467901	-0.243126
H	1.794882	0.976863	0.208458
H	-1.121054	5.445713	0.453905
H	0.532604	5.370863	0.616832
H	-1.514744	0.594738	-2.014653
H	-1.851967	2.179746	-2.222793

MXS_$^3H_4$

N	-1.205004	3.187561	0.559792
N	-0.295743	1.255184	-0.281103
N	-0.381268	4.415828	-1.278783
N	-2.615748	1.504690	-0.325215
C	-0.139137	3.953763	0.033779
C	1.120428	3.171317	0.196993
C	0.962052	1.849648	-0.038770
C	-1.347353	1.977778	-0.097864
H	2.083938	3.634131	0.301561
H	1.787365	1.162877	-0.054212
H	-1.097491	5.109744	-1.324226
H	0.440711	4.737684	-1.742641
H	-3.312599	1.891297	0.271929
H	-2.663724	0.514007	-0.417220

MXS_$^1S_6$

N	-1.676714	2.932657	0.029495
N	-0.249908	1.295210	0.753834
N	-0.865006	5.091651	0.025123
N	-2.552554	0.820001	0.451691
C	-0.523624	3.766093	0.034385
C	0.736921	3.263150	0.015750
C	0.751697	1.788250	-0.105359
C	-1.508441	1.688650	0.307452
H	1.607162	3.876164	-0.123021
H	0.754125	1.365610	-1.106632

H	-1.822415	5.340576	0.022102
H	-0.176000	5.801351	0.026807
H	-2.355636	-0.147511	0.342842
H	-3.418309	1.130455	0.074121

MXS_B_{14}

N	-1.511668	2.596590	1.161969
N	-0.605305	1.022702	-0.213106
N	-1.481536	4.463660	-0.296350
N	-1.584766	0.347688	1.861752
C	-0.905649	3.259917	0.040457
C	0.521990	2.978533	-0.213655
C	0.691671	1.646355	-0.245233
C	-1.264776	1.360130	1.002441
H	1.293932	3.726117	-0.279421
H	1.581606	1.049900	-0.273853
H	-2.172096	4.793063	0.340369
H	-0.888739	5.169209	-0.670003
H	-1.751950	0.614173	2.804598
H	-1.123082	-0.522109	1.732365

MXS_^{6}E

N	-1.375851	3.032423	0.277760
N	-0.052315	1.272943	-0.569268
N	-0.275413	5.057526	-0.032692
N	-2.353430	1.015205	-0.311853
C	-0.215299	3.695900	0.068257
C	0.962417	2.967695	-0.202806
C	1.011344	1.580207	0.301828
C	-1.252931	1.797341	-0.143386
H	1.709979	3.352505	-0.873113
H	1.907018	0.992454	0.214623
H	-1.152467	5.450914	0.224061
H	0.518894	5.575015	0.265975
H	-3.186759	1.361606	0.104464
H	-2.222044	0.030768	-0.284662

Supporting References

[1] Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992,** *97,* 2571.
[2] Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998,** *294,* 143.
[3] Schäfer, A.; Huber, C..; Ahlrichs, R. *J. Chem. Phys.* **1994,** *100,* 5829.