Efficient intersystem crossing in 2-aminopurine riboside probed by femtosecond time-resolved transient vibrational absorption spectroscopy

Electronic Supplementary Information (ESI)

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Contents

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1 Synthesis of the TBDMS-protected 2-aminopurine riboside

To a solution of 2-aminopurine riboside (1.0 g, 3.75 mmol) and imidazole (2.4 g, 35.7 mmol) in anhydrous DMF (9.1 mL) at room temperature, TBDMSCl (2.7 g, 17.9 mmol) was added. This mixture was stirred (72 h) under argon atmosphere, concentrated in vacuo and then dissolved in ethyl acetate (50 mL). The organic phase was washed with water (3 x 10 mL), dried over sodium sulfate and concentrated. Column chromatography (ethyl acetate) yielded 2',3',5'-tri-O-(tert-butyldimethylsilyl)-2-aminopurine riboside (1.3 g, 60%) as a colourless solid; R_f = 0.5 (ethyl acetate).

^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm: 8.54 (1H, s, C_6H), 8.07 (1H, s, C_8H), 5.82 (1H, d, J = 4.7 Hz, H-1'), 4.96 (2H, br s, NH2), 4.36 (1H, t, J = 4.5 Hz, H-2'), 4.16 (1H, t, J = 4.2 Hz, H-3'), 3.98 (1H, td, J = 3.7 and 2.7 Hz, H-4'), 3.86 (1H, dd, J = 11.4 and 3.6 Hz, H-5a'), 3.65 (1H, dd, J = 11.4 and 2.5 Hz, H-5b'), 0.82 (9H, br s, $C(CH_3)_3$), 0.80 (9H, br s, $C(CH_3)_3$), 0.69 (9H, br s, $C(CH_3)_3$), 0.01 (3H, br s, CH_3), 0.00 (3H, br s, CH_3), -0.03 (3H, br s, CH_3), -0.04 (3H, br s, CH_3), -0.15 (3H, br s, CH_3), -0.31 (3H, br s, CH_3);

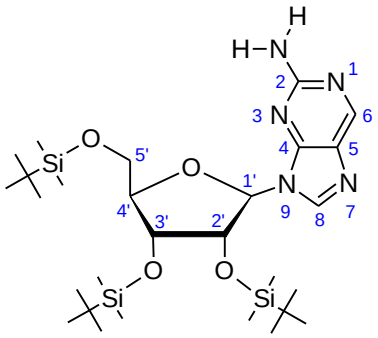
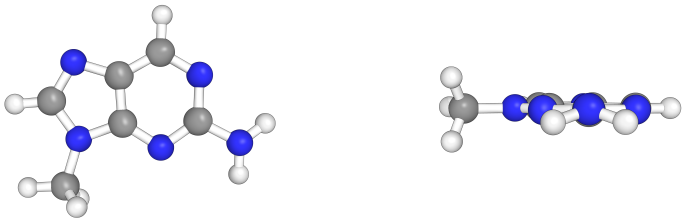


Fig. S 1: Atom numbering of the tert-butyldimethylsilyl (TBDMS) protected 2AP riboside.

2 Calculated relaxed structures of 9Me-2AP in its electronic ground state and in the excited $^1\pi\pi^*$, $^1n\pi^*$ and $^3\pi\pi^*$ states

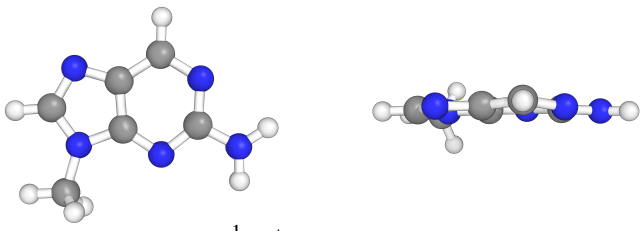
Table S 1: Cartesian coordinates for the optimized structure of 9Me-2AP in the ground electronic state at the M062X / 6-311+G** level of theory.



GS_{min} structure

atom	X / Å	Y / Å	Z / Å
N	-0.69320	-1.03900	0.00060
C	0.34970	-0.22120	-0.00100
C	0.31360	1.18120	-0.00240
C	-0.95970	1.73860	0.00290
N	-2.03410	0.96170	0.00150
C	-1.85510	-0.37750	-0.00580
N	1.59810	1.69900	0.00040
C	2.36050	0.64780	0.00250
N	1.67530	-0.55330	0.00180
H	-1.11940	2.81270	0.01160
N	-2.99710	-1.12920	-0.05580
H	3.44180	0.65980	0.00340
H	-2.91240	-2.10160	0.18870
H	-3.85320	-0.65580	0.18040
C	2.21420	-1.89860	0.00030
H	1.89960	-2.43100	0.89840
H	1.86010	-2.44150	-0.87650
H	3.30140	-1.83810	-0.02430

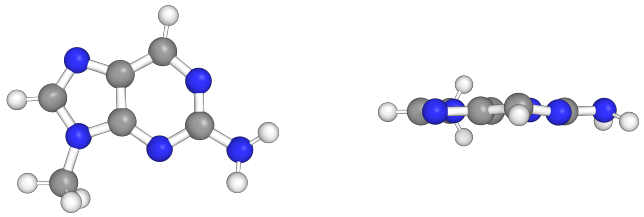
Table S 2: Cartesian coordinates for the optimized structure of 9Me-2AP in the $^1\pi\pi^*$ state at the RI-CC2 / def2-TZVPPD level of theory.



$^1\pi\pi^*_{\text{min}}$ structure

atom	X / Å	Y / Å	Z / Å
N	-0.6562444	-1.1182982	0.1111756
C	0.3573914	-0.2259930	-0.0008329
C	0.2834734	1.1912144	0.0131290
C	-1.0273705	1.7959580	0.1063167
N	-2.0888953	0.9192461	-0.0562148
C	-1.8319814	-0.4059632	0.0199180
N	1.5268826	1.7303292	-0.0140708
C	2.3614054	0.6657137	-0.0286302
N	1.7085567	-0.5244508	0.0042642
H	-1.2099263	2.8508940	-0.0384058
N	-2.9307944	-1.1934377	-0.0027764
H	3.4380297	0.7240685	-0.0604848
H	-2.8161521	-2.1920352	0.0822797
H	-3.8385390	-0.7602593	-0.0828668
C	2.2693932	-1.8610778	-0.0124458
H	1.8477662	-2.4385732	0.8071348
H	2.0334696	-2.3543297	-0.9533518
H	3.3473353	-1.7853059	0.1043620

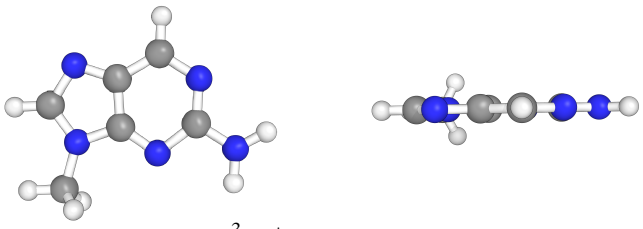
Table S 3: Cartesian coordinates for the optimized structure of 9Me-2AP in the $^1n\pi^*$ state at the RI-CC2 / def2-TZVPPD level of theory.



$^1n\pi^*_{min}$ structure

atom	X / Å	Y / Å	Z / Å
N	0.7591675	1.0328498	0.0983895
C	-0.3593971	0.2541879	0.0186917
C	-0.4280358	-1.1535798	-0.0195987
C	0.8219126	-1.8484561	0.0868728
N	1.8931881	-0.9620037	-0.0028839
C	1.9369106	0.3418791	0.0626625
N	-1.7226981	-1.5685262	-0.0839128
C	-2.4406973	-0.4448457	-0.0699292
N	-1.6493661	0.6881991	-0.0028390
H	0.9941271	-2.8860471	-0.1547364
N	3.1153345	1.0410013	0.1505593
H	-3.5151616	-0.3746327	-0.1150172
H	3.0315869	1.9907233	-0.1823126
H	3.9239397	0.5484749	-0.1973232
C	-2.0775083	2.0728501	0.0291940
H	-1.7208623	2.5516489	0.9389091
H	-1.6827989	2.6058708	-0.8336895
H	-3.1638486	2.0953993	0.0066393

Table S 4: Cartesian coordinates for the optimized structure of 9Me-2AP in the $^3\pi\pi^*$ state at the RI-CC2 / def2-TZVPPD level of theory.



$^3\pi\pi^*_{\text{min}}$ structure

atom	X / Å	Y / Å	Z / Å
N	1.0624523	0.4041203	0.0219492
C	-0.2124401	0.0419362	-0.0039726
C	-0.7619187	-1.2827166	-0.0214820
C	0.1883963	-2.3790443	-0.0097117
N	1.5172251	-2.0511483	0.0170865
C	1.8656677	-0.7821404	0.0304138
N	-2.0923527	-1.2473049	-0.0464860
C	-2.4134637	0.1009184	-0.0452770
N	-1.3009713	0.8843804	-0.0205292
H	-0.0986897	-3.4185371	-0.0202750
N	3.1796651	-0.4684388	0.0563222
H	-3.4119704	0.5022228	-0.0627829
H	3.4489715	0.4995711	0.0676276
H	3.8616740	-1.2079979	0.0656308
C	-1.2227590	2.3324041	-0.0089999
H	-0.7261819	2.6648923	0.8999588
H	-0.6518287	2.6728589	-0.8699752
H	-2.2314759	2.7340238	-0.0494974

3 Calculated electronic excitation energies for 9Me-2AP

Table S 5: Calculated vertical excitation energies (VEEs) for 9Me-2AP at the minimum energy structure of the GS and calculated energies at the minimum energy structures of the $^1\pi\pi^*$, ^{1}nπ^* and $^3\pi\pi^*$ excited states at the RI-MP2 / def2-TZVPPD (GS) resp. RI-CC2 / def2-TZVPPD (excited states) levels of theory.

	GS_{min}		$^1\pi\pi^*_{min}$	^{1}nπ^*_{min}	$^3\pi\pi^*_{min}$
	VEE / eV[b]	f[a,b]	E / eV[b]	E / eV[b]	E / eV[b]
GS	0.00	-	0.47 (0.48)	0.76 (0.84)	0.48
$^3\pi\pi^*$	3.65 (3.58)	-	3.37 (3.32)	4.01 (3.74)	3.22 (2.91)
^{3}nπ^*	4.34 (4.33)	-	4.49	3.84	4.50
$^1\pi\pi^*$	4.45 (4.35)	0.1458 (0.1374)	4.13 (4.02)	4.91 (4.84)	4.24
^{1}nπ^*	4.54 (4.55)	0.0025 (0.0031)	4.72 (4.68)	4.04 (4.01)	4.67

[a] Oscillator strength, [b] Values in parentheses from Ref. 1.

References

[1] S. Lobsiger, R. K. Sinha, M. Trachsel and S. Leutwyler, *J. Chem. Phys.*, 2011, **134**, 114307.