Conformational Preferences and Isomerization upon Excitation/Ionization of 2-Methoxypyridine and 2-N-methylaminopyridine

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Supplementary Information

Table S1 Observed cationic bands (in cm^{-1}) in the MATI spectra of *cis* 2MOP and their possible assignments[a]

Intermediate level in the S_1 state									Calc.[b]	2PyOH[c]	Anisole[d]	Assignment and description[e]
τ2	τ1 0(CH_3)τ1	16b1 0τ1	10b1	X1 0	6a1	6b1	11 0	121				
88									82			τ1 0(CH_3)
107									105			τ1 0(OCH_3)
139	141		138									τ2 0(CH_3)
		155										τ1 0(CH_3)τ1
192	196		194									τ2 0(OCH_3)
211	214	212	211						222		216	10b1 0, γ(aryl C-
				239					232		234	X1 0, β(O-CH_3)
	314	307	311									10b1 0τ1 0(CH_3)
	330	325										10b1 0τ1 0(OCH_3)
			363						364			16b1 0, γ-ring
			448		448				437	424	528	151 0, β(aryl C-O)
452		455							448		355	16a1 0, γ-ring
473												16b1 0τ1 0(OCH_3)
					488						482	X2 0, β(O-CH_3)
			581		585	581	580		573	534	431	6a1 0, β(C-C-C)
					599	597			588	596	570	6b1 0, β(C-C-C)
						668						10b1 016a1 0
	726		727									16b2 0, γ-ring
							802		797	841	764	11 0, breathing
				825								X1 06a1 0
922												16b2 0τ2 0(OCH_3)
				965								16b2 0X1 0
								995	958	989	1021	121 0, β(C-C-C)
				1037								X1 011 0
								1088	1082	1157	1108	18b1 0, β(C-H)
1128												ν1 0(O-CH_3)τ2
				1172					1129	1586	1173	9a1 0, β(C-H)
						1179						6a1 06b1 0

[a] Experimental values are the shifts from origin band 69379 cm^{-1}. [b] Calculated at ωB97XD/CC-pVTZ level, scaled by 0.96. [c] Ref 39. [d] Ref 41. [e] ν denotes bond stretching; β denotes in-plane bending; γ denotes out-of-plane bending; τ denotes the CH_3 or OCH_3 group torsion.

Table S2 Observed bands (in cm^{-1}) in the MATI spectra of *cis* 2NMP and their possible assignments[a]

Intermediate level in the S_1 state						Calc.[b]	Calc.[c]	Assignment and approximate description[d]
τ1	τ2 0(CH_3)	16b1 0	10b1 0	τ4 0(CH_3)	6b1 0			
39		39				69	73	τ1 0(CH_3)
	72		66	68				τ2 0(CH_3)
119		122	120			123	121	τ1 0($NHCH_3$)
	177		171			224	222	10b1 0, γ(aryl C-N)
			200					τ2 0($NHCH_3$)
225	240	229	236					10b1 0τ2 0(CH_3)
				248		239	223	X1 0, β(N-CH_3)
			283	282				10b1 0τ1 0($NHCH_3$)
			342	342				10b2 0, γ(aryl C-N)
		380				376	377	16b1 0, γ-ring
	440			434		455	461	16a1 0, γ-ring
				496				16a1 0τ2 0(CH_3)
					513			151 0τ4 0(CH_3)
					619	586	591	6b1 0, β(C-C-C)
	672							6a1 0τ2 0(CH_3)

[a] Experimental values are represented by the shifts from origin band 62518 cm^{-1}. [b] Calculated at unrestricted HF/CC-pVTZ level, scaled by 0.91. [c] Calculated at unrestricted ωB97XD/CC-pVTZ level, scaled by 0.96. [d] β denotes in-plane bending; γ denotes out-of-plane bending; τ denotes the CH_3 or $NHCH_3$ group torsion.

Table S3 Observed bands (in cm^{-1}) in the MATI spectra of *trans* 2NMP and the approximate assignments[a]

Intermediate level in the S_1 state								Calc.[b]	Calc.[c]	Assignment and approximate description[d]
τ2 0(CH_3)	X1 0	10b1 0τ1 0($NHCH_3$)	151 0	6a1 0	6b1 0	11 0	121 0			
79	79									τ2 0(CH_3)
182										τ2 0(CH_3)τ1 0($NHCH_3$)
200	199	198								τ2 0($NHCH_3$)
233		229						236	227	10b1 0, γ(aryl C-N)
	242							219	221	X1 0, β(N-CH_3)
		255								τ1 0(CH_3)τ2 0($NHCH_3$)
		290						294	304	10b1 0τ1 0(CH_3)
344		344						377	359	16b1 0, γ-ring
			468					454	461	151 0, β(aryl C-N)
				562	562			549	556	6a1 0, β(C-C-C)
				604	604			587	596	6b1 0, β(C-C-C)
638										6a1 0τ2 0(CH_3)
682		684								6b1 0τ2 0(CH_3)
					768					I2 0, $NHCH_3$ inversion
						803		773	793	11 0, breathing
	802							768	777	X1 06a1 0
	843							806	817	X1 06b1 0
876										11 0τ2 0(CH_3)
		948						964	955	16b1 06b1 0
							959	920	945	121 0, β(C-C-C)
							1037	1019	1047	ν1 0(N-CH_3)
				1126						6a2 0
				1165				1136	1152	6a1 06b1 0
				1207						6b2 0

[a] Experimental values are represented by the shifts from origin band 62709 cm^{-1}. [b] Calculated at unrestricted HF/CC-pVTZ level, scaled by 0.91. [c] Calculated at unrestricted ωB97XD/CC-pVTZ level, scaled by 0.96. [d] β denotes in-plane bending; γ denotes out-of-plane bending; τ denotes torsional motions of CH_3 or $NHCH_3$ group.

Table S4 The calculated geometric parameters of 2MOP conformers in the S_0, S_1 and D_0 states[a]

	cis					*trans*				
	S_0		S_1[b]	D_0		S_0		S_1[b]	D_0	
	HF	ωB97XD	CIS	UHF	UωB97XD	HF	ωB97XD	CIS	UHF	UωB97XD
Bond Length (Å)										
C1-C2	1.4003	1.4000	1.4234	1.4461	1.4379	1.3931	1.3971	1.4218	1.4476	1.4378
C2-C3	1.3646	1.3736	1.4156	1.3781	1.3728	1.3770	1.3824	1.4096	1.3752	1.3699
C3-C4	1.3950	1.3941	1.3900	1.3924	1.3881	1.3807	1.3844	1.4012	1.3955	1.3923
C4-C5	1.3671	1.3769	1.4176	1.4396	1.4319	1.3790	1.3849	1.4125	1.4411	1.4333
C5-N6	1.3301	1.3366	1.3461	1.2860	1.3029	1.3157	1.3264	1.3356	1.2808	1.2967
N6-C1	1.3011	1.3174	1.3286	1.3416	1.3440	1.3110	1.3233	1.3426	1.3497	1.3528
C1-O7	1.3280	1.3411	1.3016	1.2550	1.2840	1.3317	1.3450	1.3034	1.2553	1.2846
O7-C8	1.4072	1.4189	1.4171	1.4559	1.4547	1.3976	1.4089	1.4063	1.4444	1.4451
C8-H9	1.0806	1.0898	1.0785	1.0758	1.0862	1.0840	1.0933	1.0815	1.0779	1.0879
C8-H10	1.0806	1.0898	1.0785	1.0758	1.0862	1.0840	1.0933	1.0815	1.0779	1.0879
C8-H11	1.0786	1.0864	1.0776	1.0737	1.0826	1.0780	1.0861	1.0770	1.0737	1.0829
N6···H9	2.6596	2.6291	2.6466	2.7141	2.6850	*[c]	*	*	*	*
N6···H10	2.6596	2.6291	2.6466	2.7141	2.6850	*	*	*	*	*
Bond Angel (°)										
C1-C2-C3	117.6	117.7	118.8	118.1	118.0	117.7	117.8	119.0	118.2	118.1
C2-C3-C4	119.6	119.4	115.3	117.9	118.0	119.9	119.7	115.5	118.3	118.4
C3-C4-C5	117.4	117.9	120.8	118.8	119.5	117.0	117.5	120.4	118.5	119.2
C4-C5-N6	123.8	123.7	124.7	124.4	123.7	124.0	123.9	124.9	124.2	123.5
C5-N6-C1	118.0	117.6	114.0	117.2	116.6	118.5	118.0	114.6	117.9	117.3
N6-C1-C2	123.5	123.7	126.3	123.6	124.2	122.8	123.1	125.5	122.9	123.5
O7-C1-C2	116.6	116.7	115.1	116.3	115.8	123.5	123.7	122.1	123.1	123.4
O7-C1-N6	119.9	119.6	118.6	120.1	120.0	113.7	113.3	112.4	114.0	113.0
C8-O7-C1	119.0	117.3	120.2	122.8	120.9	120.5	118.6	122.7	125.5	123.2
C8-H9···N6	78.4	78.9	78.6	78.8	79.3	*	*	*	*	*
C8-H10···N6	78.4	78.9	78.6	78.8	79.3	*	*	*	*	*
Dihedral Angle (°)										
O7-C1-C2-C3	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
O7-C1-N6-C5	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
C8-O7-C1-N6	0.0	0.0	0.0	0.0	0.0	180.0	180.0	180.0	180.0	180.0
H9-C8-O7-C1	-60.7	-60.5	-60.6	-60.7	-60.4	-61.3	-61.3	-61.3	-61.5	-61.5
H10-C8-O7-C1	60.7	60.5	60.6	60.7	60.4	61.3	61.3	61.3	61.5	61.5

[a] All calculations are performed by using CC-pVTZ as the basis set. For the *trans* 2MOP in the S_1 state, only geometric parameters from CIS calculations are listed. [b] Only geometric parameters from CIS method are available for 2MOP in the S_1 state. [c] Terms replaced by "*" represent parameters becoming meaningless upon the isomerization from *cis* to *trans* 2MOP. For instance, the N6···H9 distance becomes very large in the *trans* 2MOP.

Table S5 The calculated geometric parameters of 2NMP in the S_0, S_1 and D_0 states[a]

	cis						*trans*					
	S_0		S_1		D_0		S_0		S_1		D_0	
	HF	ωB97XD	CIS	TD-ωB97XD	UHF	UωB97XD	HF	ωB97XD	CIS	TD-ωB97XD	UHF	UωB97XD
Bond Length (Å)												
C1-C2	1.4067	1.4077	1.4248	1.4004	1.4300	1.4264	1.4000	1.4037	1.4109	1.3928	1.4266	1.4233
C2-C3	1.3645	1.3724	1.4140	1.4332	1.3800	1.3743	1.3726	1.3786	1.4100	1.4308	1.3805	1.3746
C3-C4	1.3932	1.3936	1.3906	1.3900	1.3968	1.3877	1.3851	1.3878	1.4016	1.3972	1.3981	1.3889
C4-C5	1.3696	1.3784	1.4123	1.4101	1.4223	1.4190	1.3770	1.3839	1.4074	1.4058	1.4215	1.4202
C5-N6	1.3255	1.3331	1.3397	1.3607	1.2949	1.3031	1.3167	1.3264	1.3307	1.3576	1.2958	1.3009
N6-C1	1.3135	1.3306	1.3431	1.3434	1.3568	1.3527	1.3219	1.3368	1.3693	1.3602	1.3619	1.3597
C1-N7	1.3668	1.3680	1.3271	1.3637	1.3115	1.3300	1.3648	1.3641	1.3240	1.3571	1.3096	1.3258
N7-C8	1.4442	1.4444	1.4440	1.4369	1.4651	1.4507	1.4384	1.4374	1.4396	1.4341	1.4628	1.4508
N7-H9	0.9901	1.0023	0.9916	1.0065	0.9994	1.0111	0.9909	1.0034	0.9932	1.0091	1.0018	1.0141
C8-H10	1.0855	1.0937	1.0739	1.0845	1.0726	1.0829	1.0832	1.0956	1.0830	1.0919	1.0794	1.0895
C8-H11	1.0792	1.0881	1.0840	1.0921	1.0802	1.0897	1.0875	1.0926	1.0830	1.0919	1.0794	1.0895
C8-H12	1.0814	1.0882	1.0840	1.0921	1.0802	1.0897	1.0804	1.0872	1.0790	1.0856	1.0764	1.0844
N6···H10	2.8564	2.8447	2.3337	2.2671	2.3963	2.3643	* [b]	*	*	*	*	*
N6···H11	2.6844	2.6583	3.5330	3.5130	3.5570	3.5578	*	*	*	*	*	*
N6···H12	*	*	3.5330	3.5130	3.5570	3.5578	*	*	*	*	2.2861	2.3082
Bond Angel (°)												
C1-C2-C3	118.3	118.5	118.8	117.7	117.9	118.2	118.1	118.2	118.8	117.7	117.5	117.8
C2-C3-C4	119.7	119.5	115.6	115.6	118.5	118.4	120.1	119.8	115.6	115.5	118.9	118.7
C3-C4-C5	117.0	117.5	120.9	121.7	118.9	119.2	116.9	117.4	121.0	121.8	119.0	119.3
C4-C5-N6	124.3	124.3	124.6	123.6	123.7	123.6	124.3	124.2	124.8	123.8	123.3	123.3
C5-N6-C1	118.4	117.9	114.6	113.8	117.8	117.3	118.6	118.0	114.1	113.4	118.0	117.4
N6-C1-C2	122.1	122.3	125.5	127.6	123.2	123.4	122.0	122.3	125.6	127.8	123.4	123.6
N7-C1-C2	119.9	120.4	117.6	117.6	119.6	119.3	122.3	122.2	122.1	121.7	123.0	122.5
N7-C1-N6	118.0	117.3	116.9	114.8	117.2	117.3	115.6	115.5	112.3	110.6	113.7	114.0
C8-N7-C1	121.6	121.5	126.2	125.5	127.5	126.4	123.5	123.7	127.2	126.8	127.8	127.3
C8-N7-H9	116.0	117.1	117.3	118.1	116.1	116.7	117.3	119.1	119.3	120.7	118.3	119.0
C1-N7-H9	115.2	116.1	116.4	116.4	116.4	116.8	113.1	114.1	113.5	112.6	113.9	113.7
C8-H10···N6	73.6	73.6	103.6	105.4	102.2	102.9	*	*	*	*	*	*
C8-H11···N6	82.2	82.9	39.9	39.6	40.5	40.0	*	*	*	*	*	*
N7-H9···N6	*	*	*	*	*	*	73.1	72.6	75.5	76.2	74.4	74.1
Dihedral Angle(°)												
N7-C1-C2-C3	178.4	178.5	180.0	180.0	180.0	180.0	178.3	178.7	180.0	180.0	180.0	180.0
N7-C1-N6-C5	-178.2	-178.2	180.0	180.0	180.0	180.0	-178.4	-178.8	180.0	180.0	180.0	180.0
C8-N7-C1-N6	-13.1	-10.8	0.0	0.0	0.0	0.0	-164.6	-169.7	180.0	180.0	180.0	180.0
C8-N7-C1-H9	149.0	153.7	180.0	180.0	180.0	180.0	-151.7	-160.0	180.0	180.0	180.0	180.0
H10-C8-N7-C1	-59.4	-60.6	0.0	0.0	0.0	0.0	-67.1	-65.6	-60.7	-59.9	-60.7	-60.6
H11-C8-N7-C1	61.3	59.5	120.2	120.3	120.8	120.8	54.9	56.0	60.7	59.9	60.7	60.6

[a] All calculations are performed by using CC-pVTZ as the basis set. [b] Terms replaced by "*" represent parameters becoming meaningless upon the cis/trans isomerization.

Table S6 The pairwise steric exchange interactions dE (i,j)[a] for "disjoint" pairs of NLMOs[b] in kcal/mol

cis		*trans*			*t-Unreal*		
NLMO pair	dE (i,j)	NLMO pair	dE (i,j)	Δ [c]	NLMO pair	dE (i,j)	Δ [c]
2MOP							
σ C 1- C 2 : σ O 7- C 8	**2.96**	**σ C 1- C 2 : σ O 7- C 8**	**4.03**	**1.07**	**σ C 1- C 2 : σ O 7- C 8**	**6.76**	**3.80**
σ C 1- C 2 : n (1) N 6	11.11	σ C 1- C 2 : n (1) N 6	9.75	-1.36	σ C 1- C 2 : n (1) N 6	10.65	-0.46
σ C 1- C 2 : n (1) O 7	**3.53**	**σ C 1- C 2 : n (1) O 7**	**7.24**	**3.71**	**σ C 1- C 2 : n (1) O 7**	**8.09**	**4.56**
σ C 1- N 6 : n (1) O 7	**8.16**	**σ C 1- N 6 : n (1) O 7**	**3.21**	**-4.95**	**σ C 1- N 6 : n (1) O 7**	**1.79**	**-6.37**
σ C 1- N 6 : σ C 8- H 9	0.53	σ C 1- C 2 : σ C 8- H 9	0.59	0.06* [d]	σ C 1- C 2 : σ C 8- H 9	0.82	0.29*
σ C 1- N 6 : σ C 8- H10	0.53	σ C 1- C 2 : σ C 8- H10	0.59	0.06*	σ C 1- C 2 : σ C 8- H10	0.82	0.29*
σ C 1- N 6 : σ C 8- H11	0.37	σ C 1- C 2 : σ C 8- H11	0.23	-0.14*	σ C 1- C 2 : σ C 8- H11	0.28	-0.09*
σ O 7- C 8 : n (1) N 6	0.71	σ O 7- C 8 : σ C 2- H12	0.44	-0.27*	σ O 7- C 8 : σ C 2- H12	1.37	0.66*
σ C 8- H 9 : n (1) N 6	**2.42**	**σ C 8- H 9 : σ C 2- H12**	**2.10**	**-0.32***	**σ C 8- H 9 : σ C 2- H12**	**5.75**	**3.33***
σ C 8- H10 : n (1) N 6	**2.42**	**σ C 8- H10 : σ C 2- H12**	**2.10**	**-0.32***	**σ C 8- H10 : σ C 2- H12**	**5.75**	**3.33***
σ C 8- H11 : n (1) N 6	0.22	σ C 8- H11 : σ C 2- H12	0.37	0.15*	σ C 8- H11 : σ C 2- H12	0.80	0.58*
n (1) O 7 : n (1) N 6	0.92	n (1) O 7 : n (1) N 6	1.10	0.18			
2NMP							
σ C 1- C 2 : σ N 7- H 9	**2.65**	**σ C 1- C 2 : σ N 7- H 9**	**5.04**	**2.39**	**σ C 1- C 2 : σ N 7- H 9**	**4.99**	**2.34**
σ C 1- N 6 : σ N 7- C 8	**2.81**	**σ C 1- N 6 : σ N 7- C 8**	**4.05**	**1.24**	**σ C 1- N 6 : σ N 7- C 8**	**3.95**	**1.14**
σ N 7- H 9 : n (1) N 6	**0.27**	**σ N 7- H 9 : n (1) N 6**	**1.88**	**1.61**	**σ N 7- H 9 : n (1) N 6**	**1.29**	**1.02**
σ C 8- H11 : n (1) N 7	4.65	σ C 8- H11 : n (1) N 7	6.76	2.11	σ C 8- H11 : n (1) N 7	4.99	0.34
σ C 1- C 2 : n (1) N 6	11.40	σ C 1- C 2 : n (1) N 6	9.98	-1.42	σ C 1- C 2 : n (1) N 6	10.48	-0.92
σ C 1- N 6 : σ N 7- H 9	**5.63**	**σ C 1- N 6 : σ N 7- H 9**	**3.02**	**-2.61**	**σ C 1- N 6 : σ N 7- H 9**	**2.19**	**-3.44**
σ C 1- N 6 : σ C 8- H11	0.38	σ C 1- C 2 : σ C 8- H10	0.23	-0.15*	σ C 1- C 2 : σ C 8- H10	0.24	-0.14*
σ C 1- N 6 : σ C 8- H12	0.37	σ C 1- C 2 : σ C 8- H11	0.22	-0.15*	σ C 1- C 2 : σ C 8- H11	0.41	0.04*
σ N 7- C 8 : n (1) N 6	0.94	σ C 2- H13 : σ N 7- C 8	0.47	-0.47*	σ C 2- H13 : σ N 7- C 8	0.69	-0.25*
σ C 8- H10 : n (1) N 6	0.95	σ C 2- H13 : σ C 8- H10	0.98	0.03*	σ C 2- H13 : σ C 8- H10	1.08	0.13*
σ C 8- H11 : n (1) N 6	2.31	σ C 2- H13 : σ C 8- H11	1.47	-0.84*	σ C 2- H13 : σ C 8- H11	3.11	0.80*
σ C 8- H12 : n (1) N 6	0.25	σ C 2- H13 : σ C 8- H12	0.32	0.07*	σ C 2- H13 : σ C 8- H12	0.43	0.18*

[a] The dE (i,j) describes pairwise steric exchange interactions. Symbols "i" and "j" stand for the two NLMOs interacting with each other, respectively. [b] Only important "disjoint" pairs of NLMOs (i.e., sharing no common atom) are listed here. [c] This column shows the dE (i,j) difference between the *trans* (equilibrium and *t-Unreal*) conformers and the corresponding *cis* conformers. [d] Due to the conformational conversion, the asterisked data (being marked with "*") showing the denotation of dE (i,j) in *cis* conformer are different from those of the *trans* and corresponding *t-Unreal* species.

Table S7 The hyperconjugation interactions between methyl σC-H and SOMO orbitals on O7 (2MOP) and N7 (2NMP) atoms

s-cis		*e-cis*	
2MOP			
BD(1)C8-H9:BD*(2)C1-O7[a]	1.42	BD(1)C8-H10:BD*(2)C1-O7	1.83
BD(1)C8-H10:BD*(2)C1-O7	1.40	BD(1)C8-H11:BD*(2)C1-O7	1.83
BD*(2)C1-O7:BD*(1)C8-H9	0.15	BD*(2)C1-O7:BD*(1)C8-H10	0.10
BD*(2)C1-O7:BD*(1)C8-H10	0.14	BD*(2)C1-O7:BD*(1)C8-H11	0.10
Sum	3.11		3.86
2NMP			
BD(1)C8-H10:BD*(2)C1-N7	3.23	BD(1)C8-H11:BD*(2)C1-N7	3.60
BD(1)C8-H11:BD*(2)C1-N7	3.15	BD(1)C8-H12:BD*(2)C1-N7	3.60
BD*(2)C1-N7:BD*(1)C8-H10	0.22	BD*(2)C1-N7:BD*(1)C8-H11	0.19
BD*(2)C1-N7:BD*(1)C8-H11	0.21	BD*(2)C1-N7:BD*(1)C8-H12	0.19
Sum	6.81		7.58

[a] The term BD*(2)C1-O7 represents an unoccupied π-symmetry orbital on O7 atom formed by ionizing from the lone-pair perpendicular to the pyridine ring.