Supporting Information of “Vacuum ultraviolet spectroscopy of pyrimidine derivatives: effect of halogenation”

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Cartesian coordinates (in angstrom) of 2-chloropyrimidine in its electronic ground states, as obtained at the CAM-B3LYP/aug-cc-pVDZ+2s2p2d level of theory. See main text for the details on the 2s2p2d supplementary basis functions.

C	0.000000	0.000000	0.445914
C	0.000000	1.179831	-1.467359
C	0.000000	-1.179831	-1.467359
C	0.000000	-0.000000	-2.200295
N	0.000000	1.189423	-0.133641
N	0.000000	-1.189423	-0.133641
H	0.000000	2.155165	-1.956806
H	0.000000	-2.155165	-1.956806
H	0.000000	0.000000	-3.287821
Cl	0.000000	0.000000	-3.287821

Cartesian coordinates (in angstrom) of 2-chloropyrimidine in its first singlet excited state, as obtained at the TDDFT/CAM-B3LYP/aug-cc-pVDZ+2s2p2d level of theory. See main text for the details on the 2s2p2d supplementary basis functions.

C	0.000000	0.000000	0.515841
C	0.000000	1.192247	-1.526986
C	0.000000	-1.192247	-1.526986
C	0.000000	-0.000000	-2.242398
N	0.000000	1.119745	-0.148981
N	0.000000	-1.119745	-0.148981
H	0.000000	2.177960	-1.980603
H	0.000000	-2.177960	-1.980603
H	0.000000	0.000000	-3.331521
Cl	0.000000	0.000000	2.238920

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Table S1. Vibrational modes, harmonic and anharmonic frequencies (in cm^{-1}) for the electronic ground state of 2-chloropyrimidine, labelled according to the Mulliken nomenclature. See main text for the details on the calculations.

	Symmetry	Harmonic freq.	Anharmonic freq.	Character
1	a_1	3244.8	3115.6	H's stretching
2		3196.2	3066.6	H's stretching
3		1650.4	1613.3	ring stretching
4		1443.4	1417.5	H's rocking / ring stretching
5		1218.2	1189.8	H's rocking / C-Cl stretching
6		1106.9	1091.3	H's rocking / ring deformation
7		1020.8	1007.5	ring deformation
8		780.9	769.6	ring deformation / C-Cl stretching
9		452.1	446.9	C-Cl stretching / ring deformation
10	a_2	1020.3	993.4	H's twisting
11		422.2	414.3	ring twisting
12	b_1	1024.9	998.4	H's wagging/twisting
13		824.5	806.6	H's wagging
14		811.0	797.4	ring deformation
15		501.9	491.7	ring deformation
16		165.4	163.0	Cl wagging (out-of-plane)
17	b_2	3199.2	3086.4	H's stretching
18		1642.2	1600.1	ring stretching
19		1471.1	1446.0	ring stretching / H's rocking
20		1303.4	1286.0	H's rocking / ring stretching
21		1250.4	1235.2	ring stretching
22		1116.9	1104.3	H rocking
23		641.1	635.7	ring deformation
24		330.9	327.6	Cl rocking (in-plane)

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Table S2. Vibrational modes, harmonic and anharmonic frequencies (in cm^{-1}) for the first singlet excited state of 2-chloropyrimidine, labelled according to the Mulliken nomenclature. See main text for the details on the calculations.

	Symmetry	Harmonic freq.	Anharmonic freq.	Character
1	a_1	3267.7	3135.8	H's stretching
2		3227.3	3098.2	H's stretching
3		1545.3	1511.8	ring stretching
4		1442.3	1414.6	H's rocking / ring deformation
5		1182.8	1155.9	H's rocking / ring deformation
6		1075.7	1060.4	H's rocking
7		970.8	958.1	ring deformation
8		762.0	750.9	ring deformation / C-Cl stretching
9		440.3	435.3	C-Cl stretching / ring deformation
10	a_2	598.0	582.2	H's twisting
11		242.0	242.9	ring twisting
12	b_1	934.5	912.0	H wagging
13		713.5	699.2	H's wagging / ring deformation
14		566.4	554.1	ring deformation / H's wagging
15		480.0	471.1	H's wagging
16		188.1	185.2	Cl wagging (out-of-plane)
17	b_2	3254.2	3139.5	H's stretching
18		1386.5	1365.9	ring stretching
19		1346.5	1326.6	H's rocking / ring stretching
20		1245.2	1223.4	H's rocking
21		1044.8	1031.8	H rocking / ring stretching
22		896.3	879.7	ring deformation
23		414.1	409.8	ring deformation
24		245.4	237.1	Cl rocking (in-plane)

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Table S3. Calculated vertical excitation energies (ΔE), in eV, and vertical oscillator strengths (f_0) of 2-chloropyrimidine, 2-bromopyrimidine[a] and pyrimidine, computed at the TDDFT/CAM-B3LYP/aug-cc-pVDZ+2s2p2d level of theory. Only the states with the largest oscillator strengths for each band are shown. The character of the transition is given by the dominant hole and particle natural transition orbitals and their corresponding occupation numbers, whose signs are inferred from the phases of the TDDFT amplitudes. The colors help to distinguish the different transitions.

[a] Int. J. Mol. Sci., 2021, **22**, 6460.

Experimental				Theoretical			
Band	Mol.	Band max.	Peak Cross section	State	ΔE	f_0	Character
I	Pyr	4.18	1.2	$1\,^1B_1$	4.54	0.0054	0.99 $n_-(b_2)$ $\pi^*(a_2)$
	2ClPyr	4.27	1.0	$1\,^1B_1$	4.58	0.0043	0.99 $n_-(b_2)$ $\pi^*(a_2)$
	2BrPyr	4.25	0.9	$1\,^1B_1$	4.55	0.0037	0.99 $n_-(b_2)$ $\pi^*(a_2)$
II	Pyr	5.22	5.9	$1\,^1B_2$	5.85	0.0460	0.76 $\pi(b_1)$ $\pi^*(a_2)$
	2ClPyr	4.91	7.8	$1\,^1B_2$	5.50	0.0447	0.87 $\pi(b_1)$ $\pi^*(a_2)$
	2BrPyr	4.85	6.5	$1\,^1B_2$	5.40	0.0343	0.89 $\pi(b_1)$ $\pi^*(a_2)$
III	Pyr	6.69	16.0	$2\,^1A_1$	6.69	0.0423	0.74 $\pi(b_1)$ $\pi^*(b_1)$ - 0.23 $\pi(a_2)$ $\pi^*(a_2)$
	2ClPyr	6.18	33.5	$2\,^1A_1$	6.29	0.2187	0.92 $\pi(b_1)$ $\pi^*(b_1)$
	2BrPyr	5.91	36.9	$2\,^1A_1$	6.03	0.2446	0.95 $\pi(b_1)$ $\pi^*(b_1)$
IV	Pyr	7.48	116.1	$3\,^1A_1$	7.34	0.1062	0.84 $n_-(b_2)$ $3p_y(b_2)$
				$3\,^1B_2$	7.39	0.0539	0.97 $n_-(b_2)$ $3p_z(a_1)$
				$4\,^1A_1$	7.59	0.3366	0.67 $\pi(a_2)$ $\pi^*(a_2)$ + 0.24 $\pi(b_1)$ $\pi^*(b_1)$
				$4\,^1B_2$	7.81	0.4020	0.67 $\pi(a_2)$ $\pi^*(b_1)$ - 0.21 $\pi(b_1)$ $\pi^*(a_2)$
	2ClPyr	7.15	77.6	$3\,^1A_1$	7.41	0.3697	0.76 $\pi(a_2)$ $\pi^*(a_2)$ + 0.14 $\pi_{Cl}(b_1)$ $\pi^*(b_1)$
				$3\,^1B_2$	7.44	0.0641	0.46 $\pi(a_2)$ $\pi^*(b_1)$ - 0.32 $\pi_{Cl}(b_1)$ $\pi^*(a_2)$
		7.93	60.4	$6\,^1B_2$	8.15	0.2733	0.54 $\pi_{Cl}(b_1)$ $\pi^*(a_2)$ + 0.29 $\pi(a_2)$ $\pi^*(b_1)$
				$6\,^1A_1$	8.24	0.0674	0.75 $\pi_{Cl}(b_1)$ $\pi^*(b_1)$
	2BrPyr	7.09	60.2	$3\,^1A_1$	7.24	0.1241	0.60 $\pi(a_2)$ $\pi^*(a_2)$ + 0.33 $\pi_{Br}(b_1)$ $\pi^*(b_1)$
		7.68	86.8	$5\,^1A_1$	7.75	0.1902	0.61 $\pi(b_1)$ $3p_x(b_1)$ - 0.23 $\pi_{Br}(b_1)$ $\pi^*(b_1)$
		8.04	99.9	$6\,^1A_1$	7.87	0.2166	0.45 $\pi(b_1)$ $3p_x(b_1)$ + 0.30 $\pi_{Br}(b_1)$ $\pi^*(b_1)$
				$8\,^1B_2$	8.00	0.4315	0.51 $\pi(a_2)$ $\pi^*(b_1)$ + 0.33 $\pi_{Br}(b_1)$ $\pi^*(a_2)$

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