

SUPPORTING INFORMATION

From 2,4-Dimethoxypyrimidine to 1,3-Dimethyluracil: Isomerization and Hydrogenation Enthalpies and Non- Covalent Interactions.

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Combustion calorimetry results

In table S2 is presented the details of all combustion experiments performed for 2,4-dimethoxypyrimidine.

The symbols presented in these tables have the following meanings: $m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of fuse (cotton) used in each experiment; $m''(\text{polyethylene})$ is the mass of polyethylene used in each experiment; T_i is the initial temperature; T_f is the final temperature; ΔT_{ad} is the corrected temperature rise for adiabatic conditions; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; $\varepsilon(\text{calor})_{\text{corr.}}$ is the corrected energy equivalent of the calorimeter for the amount of water used; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{cotton})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{polyethylene})$ is the energy of combustion of polyethylene; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electrical energy for ignition; ΔU_{Σ} is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion

TABLE S1Standard ($p^\circ = 0.1$ MPa) massic energy of combustion of 2,4-dimethoxypyrimidine, at $T = 298.15$ K.

Experiment	1	2	3	4	5	6
$m(\text{cpd}) / \text{g}$	0.31034	0.43199	0.44019	0.36209	0.20454	0.37541
$m'(\text{fuse}) / \text{g}$	0.00198	0.00171	0.00184	0.00202	0.00205	0.00218
$m''(\text{polyethylene}) / \text{g}$	0.22270	0.26421	0.30080	0.27503	0.20072	0.28303
T_i / K	298.1512	298.1516	298.1505	298.1507	298.1519	298.1506
T_f / K	299.3599	299.6465	299.7590	299.5780	299.1515	299.6208
$\Delta T_{\text{ad}} / \text{K}$	1.09784	1.39452	1.51276	1.32494	0.88012	1.36723
$\varepsilon_i / \text{J} \cdot \text{K}^{-1}$	15.40	15.65	15.74	15.58	15.21	15.62
$\varepsilon_f / \text{J} \cdot \text{K}^{-1}$	16.20	16.62	16.76	16.53	15.88	16.60
$\varepsilon(\text{calor})_{\text{corr.}} / \text{J} \cdot \text{K}^{-1}$	15986.96	15988.22	15986.54	15984.03	15989.89	15989.89
$\Delta m(\text{H}_2\text{O}) / \text{g}$	−0.2	+0.1	−0.3	−0.9	+0.5	+0.5
$-\Delta U(\text{IBP})^a / \text{J}$	17567.95	22318.00	24208.00	21198.59	14086.87	21883.38
$\Delta U(\text{cotton}) / \text{J}$	32.16	27.77	29.88	32.80	33.29	35.40
$\Delta U(\text{polyethylene}) / \text{J}$	10307.00	12228.09	13921.68	12728.99	9289.92	13099.21
$\Delta U(\text{HNO}_3) / \text{J}$	29.79	41.97	49.19	37.61	21.79	38.33
$\Delta U(\text{ign}) / \text{J}$	0.96	1.07	1.15	1.19	1.13	1.17
$\Delta U_\Sigma / \text{J}$	8.26	11.19	11.86	9.99	5.97	10.38
$-\Delta_c u^\circ / \text{J} \cdot \text{g}^{-1}$	23170.52	23169.47	23161.34	23168.83	23149.02	23174.82

$$-\langle \Delta_c u^\circ \rangle = (23165.7 \pm 3.8) \text{ J} \cdot \text{g}^{-1}$$

^a $\Delta U(\text{IBP})$ includes $\Delta U(\text{ign})$.

Table S2Enthalpies at $T = 298.15$ K calculated with the G3 computational method.

Compound	$H(298.15)$ / hartree
Benzene	-232.046729
<i>Cis</i> -2-methoxypyridine	-362.545357
4-Methoxypyridine	-362.535518
2,4-Dimethoxypyrimidine	-493.053962
1,3-Dimethyluracil	-493.095082
1,3-Dimethyluracil (PCM-water)	-493.112004
1,3-Dimethyl-5,6-dihidrouracil	-494.286001
1,3-Dimethyl-5,6-dihidrouracil (PCM-water)	-494.300528

Table S3Enthalpies at $T = 298.15$ K calculated with CBS-APNO computational method.

Compound	$H(298.15)$ / hartree
Benzene	-232.131262
<i>Cis</i> -2-methoxypyridine	-362.679136
4-Methoxypyridine	-362.669128
2,4-Dimethoxypyrimidine	-493.237705
1,3-Dimethyluracil	-493.278821

Table S4

Electronic energies calculated at the M06-2X/6-311++G(d,p) level of theory.

Compound	E_{el} / hartree
2,4-Dimethoxypyrimidine	-493.340041
2,4-Dimethoxypyrimidine staking dimer	-986.689793
2,4-Dimethoxypyrimidine <i>in plane</i> dimer	-986.685148
1,3-Dimethyluracil	-493.380235
1,3-Dimethyluracil staking dimer	-986.778625
1,3-Dimethyluracil <i>in plane</i> dimer	-986.769182

Table S6

Standard molar enthalpies of formation, the gaseous phase, at $T = 298.15$ K, for several compounds.

Compound	$\frac{\Delta_f H_m^\circ(\text{g})}{\text{kJ} \cdot \text{mol}^{-1}}$
Benzene [1]	82.6 ± 0.7
2-Methoxypyridine [2]	-42.7 ± 1.9
4-Methoxypyridine [2]	-18.2 ± 1.8

[1] Pedley, J.B. Thermochemical Data and Structures of Organic Compounds, Thermodynamics Research Center, College Station, Texas, 1994.

[2] Amaral, L.M.P.F.; Ribeiro da Silva, M.A.V. *J. Chem. Thermodynamics* **2012**, *48*, 65-69.