

Supplementary Materials

Table S1. Results of combustion experiments at $T = 298.15$ K of furfurylamine.

| Experiment n ^o | 1 | 2 | 3 | 4 | 5 | 6 |
|--|----------|----------|----------|----------|----------|----------|
| $m'(\text{cpd}) / \text{g}$ | 0.63493 | 0.66633 | 0.45132 | 0.69286 | 0.63371 | 0.72167 |
| $m''(\text{fuse}) / \text{g}$ | 0.00226 | 0.00250 | 0.00231 | 0.00235 | 0.00230 | 0.00269 |
| $m''(\text{Melinex}^{\text{®}}) / \text{g}$ | 0.05952 | 0.05879 | 0.05788 | 0.05778 | 0.06247 | 0.05581 |
| $\Delta T_{\text{ad}} / \text{K}$ | 1.27134 | 1.32875 | 0.92690 | 1.37676 | 1.27360 | 1.42755 |
| $\varepsilon / \text{J}\cdot\text{K}^{-1}$ | 16.18 | 16.19 | 15.71 | 16.32 | 16.16 | 16.34 |
| $\Delta m(\text{H}_2\text{O}) / \text{g}$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $-\Delta U(\text{IBP}) / \text{J}^{\text{a}}$ | 20242.94 | 21157.22 | 14757.91 | 21921.83 | 20278.87 | 22730.60 |
| $\Delta U(\text{Melinex}^{\text{®}}) / \text{J}$ | 1363.15 | 1346.47 | 1325.68 | 1323.17 | 1430.77 | 1278.16 |
| $\Delta U(\text{fuse}) / \text{J}$ | 36.70 | 40.60 | 37.51 | 38.16 | 37.35 | 43.69 |
| $\Delta U(\text{HNO}_3) / \text{J}$ | 42.09 | 45.43 | 31.34 | 45.67 | 44.72 | 46.80 |
| $\Delta U(\text{ign}) / \text{J}$ | 0.96 | 0.85 | 0.94 | 0.90 | 0.99 | 0.91 |
| $\Delta U_{\Sigma} / \text{J}$ | 12.32 | 12.88 | 8.84 | 13.41 | 12.34 | 13.93 |
| $-\Delta_c u^{\circ} / \text{J}\cdot\text{g}^{-1}$ | 29591.73 | 29582.70 | 29589.96 | 29589.56 | 29593.49 | 29581.42 |

$$-\langle \Delta_c u^{\circ} \rangle = 29588.1 \pm 2.0 \text{ J}\cdot\text{g}^{-1\text{b}}$$

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

^b Mean value and standard deviation of the mean.

Table S2. Results of combustion experiments at $T = 298.15$ K of 5-methylfurfurylamine.

| Experiment n ^o | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|----------|----------|----------|----------|----------|----------|----------|----------|
| $m(\text{cpd}) / \text{g}$ | 0.60107 | 0.44562 | 0.56344 | 0.48083 | 0.50597 | 0.51508 | 0.41075 | 0.48409 |
| $m'(\text{fuse}) / \text{g}$ | 0.00273 | 0.00286 | 0.00296 | 0.00266 | 0.00257 | 0.00283 | 0.00293 | 0.00270 |
| $m''(\text{Melinex}^{\text{®}})/\text{g}$ | 0.05266 | 0.05166 | 0.05299 | 0.05411 | 0.05599 | 0.05413 | 0.05633 | 0.05235 |
| $\Delta T_{\text{ad}} / \text{K}$ | 1.27283 | 0.96234 | 1.19820 | 1.03607 | 1.08872 | 1.10431 | 0.90054 | 1.04019 |
| $\varepsilon / (\text{J}\cdot\text{K}^{-1})$ | 16.26 | 15.84 | 16.16 | 15.91 | 16.02 | 16.02 | 15.74 | 15.93 |
| $\Delta m(\text{H}_2\text{O}) / \text{g}$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 |
| $-\Delta U(\text{IBP}) / \text{J}^{\text{a}}$ | 20280.09 | 15332.46 | 19090.94 | 16507.20 | 17346.31 | 17595.02 | 14347.72 | 16572.97 |
| $\Delta U(\text{Melinex}^{\text{®}}) / \text{J}$ | 1205.97 | 1183.13 | 1213.51 | 1239.33 | 1282.28 | 1239.78 | 1290.04 | 1198.89 |
| $\Delta U(\text{fuse}) / \text{J}$ | 44.34 | 46.45 | 48.07 | 43.20 | 41.74 | 45.96 | 47.58 | 43.85 |
| $\Delta U(\text{HNO}_3) / \text{J}$ | 38.03 | 27.16 | 35.40 | 32.18 | 30.81 | 33.67 | 26.75 | 31.22 |
| $\Delta U(\text{ign}) / \text{J}$ | 0.75 | 0.73 | 0.65 | 0.82 | 0.72 | 0.88 | 0.71 | 0.72 |
| $\Delta U_{\Sigma} / \text{J}$ | 11.21 | 8.36 | 10.52 | 9.03 | 9.53 | 9.65 | 7.84 | 9.06 |
| $-\Delta_c u^{\circ} / \text{J}\cdot\text{g}^{-1}$ | 31577.92 | 31568.06 | 31562.26 | 31577.61 | 31586.75 | 31579.48 | 31589.80 | 31584.93 |

$$-\langle \Delta_c u^{\circ} \rangle = 31578.4 \pm 3.3 \text{ J}\cdot\text{g}^{-1\text{b}}$$

^a ΔU (IBP) already includes the ΔU (ign).

^bMean value and standard deviation of the mean.

$m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of the fuse (cotton) used in each experiment; $m''(\text{Melinex}^{\text{®}})$ is the mass of the Melinex[®] bags; ΔT_{ad} is the corrected temperature rise; ε is the energy equivalent of the contents in the final state; $\Delta m(\text{H}_2\text{O})$ 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; $\Delta U(\text{Melinex}^{\text{®}})$ is the energy of combustion of the Melinex[®] bags; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electric energy for the ignition; ΔU_{Σ} is the standard state correction; $\Delta_c u^{\circ}$ is the standard massic energy of combustion.

Table S3. Absolute enthalpies, $H_{298.15K}$, Gibbs energies, $G_{298.15K}$, relative free energies and Boltzmann populations in gas-phase, calculated at G3 level of theory. 1 a. u. (Hartree) corresponds to 2625.50 kJ·mol⁻¹. *Calculated from $e^{-[\Delta G_{rel}/RT]}/\sum_i^n e^{-[\Delta G_{rel}/RT]}$

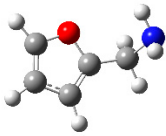
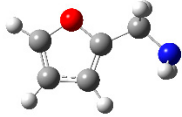
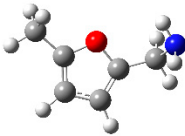
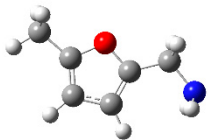
| Structure | $\frac{H_{298.15K}}{\text{Hartree}}$ | $\frac{G_{298.15K}}{\text{Hartree}}$ | $\frac{\Delta H_{298.15K}}{\text{kJ}\cdot\text{mol}^{-1}}$ | $\frac{\Delta G_{298.15K}}{\text{kJ}\cdot\text{mol}^{-1}}$ | Boltzmann relative population (%)* |
|--|--------------------------------------|--------------------------------------|--|--|--|
| Furfurylamine | | | | | |
|  Gauche form | -324.442355 | -324.480514 | 0.00 | 0.00 | 75.7 |
|  Syn form | -324.441387 | -324.479443 | 2.54 | 2.81 | 24.3 |
| 5-Methylfurfurylamine | | | | | |
|  Gauche form | -363.720879 | -363.762991 | 0.00 | 0.00 | 77.0 |
|  Syn form | -363.71982 | -363.761852 | 2.78 | 2.99 | 23.0 |

Table S4. Computed enthalpies of reaction, $\Delta_r H_m^\circ$, and formation, $\Delta_f H_m^\circ$, in the gaseous state, of furfurylamine, using G3 at $T = 298.15$ K

| Reaction | | $\frac{\Delta_r H_m^\circ(g)}{\text{kJ}\cdot\text{mol}^{-1}}$ | $\frac{-\Delta_f H_m^\circ(g)}{\text{kJ}\cdot\text{mol}^{-1}}$ |
|--|-----|---|--|
| Furfurylamine + 2-methylfuran \rightarrow 5-methylfurfurylamine + furan | (1) | 0.2 | 39.8 |
| Furfurylamine + ethane \rightarrow ethylamine + 2-methylfuran | (2) | -2.5 | 37.5 |
| Furfurylamine + methane \rightarrow ethylamine + furan | (3) | 32.8 | 40.7 |
| Furfurylamine + benzene \rightarrow aniline+ 2-methylfuran | (4) | -35.5 | 36.7 |
| Furfurylamine + benzaldehyde \rightarrow benzamide + 2-methylfuran | (5) | -100.0 | 40.6 |
| Furfurylamine + formaldehyde \rightarrow methylamine + furaldehyde | (6) | -27.5 | 38.3 |
| Furfurylamine + toluene \rightarrow 2,6-dimethylaniline + furan | (7) | -27.7 | 38.6 |
| $\langle \Delta_f H_m^\circ(g) \rangle (G3) = (-38.9 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1a}$ | | | |

^aMean and standard deviation.**Table S5.** Computed enthalpies of reaction, $\Delta_r H_m^\circ$, and formation, $\Delta_f H_m^\circ$, in the gaseous state, of 5-methylfurfurylamine, using G3 at $T = 298.15$ K

| Reaction | | $\frac{\Delta_r H_m^\circ(g)}{\text{kJ}\cdot\text{mol}^{-1}}$ | $\frac{-\Delta_f H_m^\circ(g)}{\text{kJ}\cdot\text{mol}^{-1}}$ |
|--|-----|---|--|
| 5-Methylfurfurylamine + furan \rightarrow furfurylamine + 2-methylfuran | (1) | -0.2 | 84.9 |
| 5-Methylfurfurylamine + methane \rightarrow ethylamine + 2-methylfuran | (2) | 32.7 | 82.2 |
| 5-Methylfurfurylamine + benzene \rightarrow aniline + 2,5-dimethylfuran | (3) | -35.1 | 84.3 |
| 5-Methylfurfurylamine + phenol \rightarrow 2-aminophenol+ 2,5-dimethylfuran | (4) | -34.4 | 79.9 |
| 5-Methylfurfurylamine + formaldehyde \rightarrow furaldehyde + ethylamine | (5) | -11.5 | 78.6 |
| 5-Methylfurfurylamine + formaldehyde \rightarrow methylamine + 5-methylfuraldehyde | (6) | -30.8 | 80.8 |
| 5-Methylfurfurylamine + benzene \rightarrow 2,6-dimethylaniline + furan | (7) | -16.6 | 82.5 |
| $\langle \Delta_f H_m^\circ(g) \rangle (G3) = (-81.9 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1a}$ | | | |

^aMean and standard deviation.

Table S6. G3 computed enthalpies for furfurylamine and 5-methylfurfurylamine and for the auxiliary molecules used in the gas-phase reactions and standard molar enthalpies of formation, at $T = 298.15$ K, taken from the literature.

| Compound | -G3 Enthalpy ($T = 298.15$ K) / a.u. ^a | $\Delta_f H_m^0(g)$ / kJ·mol ⁻¹ |
|------------------------|---|--|
| Furfurylamine | 324.442123 ^b | -43.5 ± 1.4^c |
| 5-Methylfurfurylamine | 363.720635 ^b | -81.2 ± 1.7^c |
| Benzene | 232.04673 | 82.9 ± 0.9 [1] |
| Aniline | 287.368547 | 87.1 ± 1.1 [2] |
| 2,6-Dimethylaniline | 365.91845 | 18.6 ± 1.5 [3] |
| Benzaldehyde | 345.31516 | -36.7 ± 2.8 [2] |
| Toluene | 271.321035 | 50.1 ± 1.1 [1] |
| Benzamide | 400.661539 | -100.9 ± 1.2 [4] |
| Methane | 40.45381 | -74.8 ± 0.34 [5] |
| Ethane | 79.718911 | -84.0 ± 0.4 [5] |
| Methylamine | 95.75736 | -23.4 ± 1.0 [2] |
| Ethylamine | 135.028174 | -47.5 ± 0.6 [2] |
| Formaldehyde | 114.427242 | -108.6 ± 0.5 [2] |
| Furan | 229.855245 | -34.8 ± 0.7 [2] |
| 2-Methylfuran | 269.133828 | -76.4 ± 1.2 [6] |
| 2,5-Dimethylfuran | 308.412174 | -123.5 ± 1.0 [7] ^d |
| Furaldehyde | 343.124092 | -151.0 ± 4.6 [2] |
| 5-Methyl-2-furaldehyde | 382.403866 | -196.8 ± 1.8 [6] |

^a All energies are in Hartrees. (1 Hartree = 2625.5 kJ·mol⁻¹); ^b Calculated considering the thermal populations in table S5; ^c This work; ^dL.M.P.F. Amaral, Calvet determination of enthalpy of vaporization, personal communication (2004).

Table S7. Purification details of furfurylamine and 5-methylfurfurylamine.

| Chemical name | CAS | Provenance | Initial mass fraction purity | Purification method | Final mass fraction purity | Analysis method |
|--------------------------|------------|----------------|------------------------------|---------------------|----------------------------|--------------------------|
| 2-Furfurylamine | 617-89-0 | Sigma-Aldrich® | 0.99 | Distillation | 0.99998 | CO ₂ recovery |
| 5-Methyl-2-furfurylamine | 14003-16-0 | Sigma-Aldrich® | 0.97 | Distillation | 0.99984 | CO ₂ recovery |

Table S8. Standard molar heat capacities, in the gaseous phase, of furfurylamine and 5-methylfurfurylamine derived from statistical thermodynamics using the vibrational frequencies calculated at the basis B3LYP/6-31G(2df,p) level of theory (scaled by a factor of 0.965)^a [8].

| T / K | $C_{p,m}^o$ (g) / J·K ⁻¹ ·mol ⁻¹ | |
|--------|--|-----------------------|
| | Furfurylamine | 5-Methylfurfurylamine |
| 100 | 52.79 | 65.69 |
| 150 | 64.05 | 81.85 |
| 200 | 77.75 | 98.62 |
| 250 | 93.85 | 117.16 |
| 298.15 | 110.43 | 136.04 |
| 300 | 111.07 | 136.77 |
| 350 | 128.13 | 156.35 |
| 400 | 144.21 | 175.01 |
| 450 | 158.92 | 192.31 |
| 500 | 172.17 | 208.07 |
| 550 | 184.02 | 222.32 |
| 600 | 194.64 | 235.20 |

^a The C_p of each conformer was obtained considering the Boltzmann relative population.

$C_{p,m}^o$ (g) = f(T), determined used to correct $\Delta_{l,298.15K}^{g,T} H_m^o$ to 298.15 K, using the equation:

$$\Delta_l^g H_m^o(298.15K) = \Delta_{l,298.15K}^{g,T} H_m^o - \int_{298.15K}^T C_{p,m}^o(g) dT \quad (S1)$$

Furfurylamine

$$\frac{C_{p,m}^o}{J \cdot mol^{-1} \cdot K^{-1}} = -7.72952 \times 10^{-7} (T/K)^3 + 7.42328 \times 10^{-4} (T/K)^2 + 9.61589 \times 10^{-2} (T/K) + 35.913 \quad (S2)$$

5-Methylfurfurylamine

$$\frac{C_{p,m}^o}{J \cdot mol^{-1} \cdot K^{-1}} = -6.45289 \times 10^{-7} (T/K)^3 + 5.82130 \times 10^{-4} (T/K)^2 + 2.09057 \times 10^{-1} (T/K) + 39.237 \quad (S3)$$

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