SUPPORTING INFORMATION

2- and 3-Acetylpyrroles: A Combined Calorimetric and Computational Study

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This supplementary information includes detailed data of the effusion orifices (diameter and Clausing factors) of the Knudsen effusion apparatus (Knudsen-2); the data and the details of all the combustion calorimetry experiments for the 2- and 3-acetylpyrroles; comparison of selected structural parameters for 2- and 3-acetylpyrroles calculated with different computational approaches; G3(MP2)//B3LYP enthalpies (energies plus thermal corrections for T=298.15 K) for the 2- and 3-acetylpyrroles, for the auxiliary molecules and for the atoms used in the several working reactions; standard molar enthalpies of formation, at T = 298.15 K, taken from the literature; comparison between the experimental and computed B3LYP/6-311+G(2d,2p) and MP2/6-311+G(2d,2p) gas-phase enthalpies of formation of 2- and 3-acetylpyrroles, at T = 298.15 K; G3(MP2)//B3LYP computed proton affinities, PA, at T = 298.15 K for pyrrole and for the 2- and 3-acetylpyrroles.

Data (areas and Clausing factors) of the effusion orifices of the Knudsen effusion apparatus (Knudsen-2)

A_o is the area of the effusion orifice and w_0 is the transmission probability factor (Clausing factor) calculated by means of the following equation

$$w_o = \{1 + (3l/8r)\}^{-1}$$

Table S1

Areas and transmission probability factors for the platinum orifices of the Knudsen effusion apparatus – 3-acetylpyrrole; $l = 0.0125$ mm

	Orifice number	Orifice diameter $2r$ / mm	l/r	A_o / mm^2	w_o
Small orifices	A1	0.7998	0.0313	0.502	0.988
	A2	0.8050	0.0311	0.509	0.988
	A3	0.8160	0.0306	0.523	0.989
Medium orifices	B4	0.9924	0.0252	0.774	0.991
	B5	0.9986	0.0250	0.783	0.991
	B6	1.0040	0.0249	0.792	0.991
Large orifices	C7	1.1830	0.0211	1.099	0.992
	C8	1.1970	0.0209	1.125	0.992
	C9	1.2000	0.0208	1.131	0.992

Combustion calorimetry results

Tables S2 and S3 register the details of all experimental determinations of the standard massic energies of combustion of the compounds studied: 2-acetylpyrrole and 3-acetylpyrrole. The symbols presented in these tables have the following meaning:

m (CO_2, total) is the mass of CO_2 recovered in each combustion; m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of the fuse (cotton) used in each experiment; m''(n-hex) is the mass of n-hexadecane used as auxiliary of combustion; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of the contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes ΔU(ignition); ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(n-hex) is the energy of combustion of n-hexadecane used as auxiliary of combustion; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electric energy for the ignition; ΔU_{Σ} is the standard state correction; $\Delta_c u^o$ is the standard massic energy of combustion.

Table S2

Standard (p^{o} = 0.1 MPa) massic energy of combustion of 2-acetylpyrrole, at T = 298.15 K

	1	**2**	**3**	**4**	**5**	**6**	**7**
m (CO$_2$, total) / g	1.77938	1.73035	---	1.88140	1.91186	1.89927	1.91577
m(cpd) / g	0.41180	0.44512	0.44676	0.44200	0.43453	0.44344	0.44744
m'(fuse) / g	0.00290	0.00268	0.00270	0.00229	0.00303	0.00240	0.00267
m''(n-hex) / g	0.25027	0.20869	0.26071	0.25989	0.27512	0.26447	0.26652
ΔT_{ad} / K	1.49549	1.43380	1.58981	1.57802	1.61002	1.59439	1.60826
ε_{f} / J·K^{-1}	16.47	16.33	16.64	16.62	16.68	16.64	16.67
Δm(H$_2$O) / g	0	–0.1	0	0	0	–0.1	–0.1
$-\Delta U$(IBP) [a] / J	23970.41	22980.83	25482.55	25293.74	25806.94	25555.74	25778.17
ΔU(fuse) / J	47.10	43.52	43.85	37.19	49.21	38.98	43.36
ΔU(n-hex) / J	11811.06	9848.70	12303.90	12265.15	12983.86	12481.10	12577.96
ΔU(HNO$_3$) / J	35.14	35.14	33.27	33.75	33.75	34.01	34.01
ΔU(ign) / J	1.20	1.14	1.21	1.01	0.84	0.77	0.71
ΔU_{Σ} / J	10.91	11.00	11.83	11.71	11.79	11.80	11.93
$-\Delta_{\mathrm{c}}u^{\mathrm{o}}$ / J·g^{-1}	29301.12	29301.02	29299.18	29289.46	29292.18	29293.37	29302.05

[a] ΔU(IBP) includes ΔU(ign).

Table S3

Standard (p^o = 0.1 MPa) massic energy of combustion of 3-acetylpyrrole, at T = 298.15 K

	1	**2**	**3**	**4**	**5**	**6**
m (CO_2, total) / g	1.66994	1.65634	1.68636	1.61618	---	1.60219
m(cpd) / g	0.35128	0.32383	0.31878	0.33601	0.32645	0.33196
m'(fuse) / g	0.00314	0.00246	0.00312	0.00299	0.00279	0.00274
m''(n-hex) / g	0.26204	0.27939	0.29262	0.25672	0.25507	0.25550
ΔT_{ad} / K	1.41915	1.41931	1.44901	1.37527	1.35234	1.36412
ε_f / J·K^{-1}	16.63	16.68	16.76	16.59	16.56	16.55
$\Delta m(H_2O)$ / g	0.3	0	0.1	0	0	0.1
$-\Delta U$(IBP) [a] / J	22749.15	22749.62	23227.01	22043.96	21676.51	21865.86
ΔU(fuse) / J	50.99	39.95	50.67	48.56	45.31	44.50
ΔU(n-hex) / J	12355.50	13173.16	13797.26	12104.35	12026.46	12046.76
$\Delta U(HNO_3)$ / J	31.30	27.16	25.21	27.40	27.22	29.25
ΔU(ign) / J	0.80	1.18	0.59	0.78	0.63	0.67
ΔU_Σ / J	9.81	9.49	9.59	9.43	9.20	9.31
$-\Delta_c u^o$ / J·g^{-1}	29325.75	29335.95	29312.63	29327.16	29310.22	29328.96

[a] ΔU(IBP) includes ΔU(ign).

Table S4

Selected structural parameters for 2- and 3-acetylpyrroles calculated with different computational approaches.[a]

	2-Acetylpyrrole				3-Acetylpyrrole		
	B3LYP /6-31G(d)	B3LYP / 6-311+G(2d,2p)	MP2 / 6-311+G(2d,2p)	Exptl.[b]	B3LYP/6-31G(d)	B3LYP / 6-311+G(2d,2p)	MP2 / 6-311+G(2d,2p)
N-H	1.011	1.007	1.008	0.9146	1.009	1.004	1.005
N-C2	1.379	1.375	1.369	1.370	1.362	1.359	1.363
C2-C3	1.393	1.389	1.399	1.380	1.388	1.384	1.391
C3-C4	1.413	1.410	1.410	1.393	1.434	1.432	1.426
C4-C5	1.389	1.385	1.393	1.366	1.373	1.369	1.381
C5- N	1.359	1.356	1.362	1.349	1.382	1.379	1.375
C2-C6	1.460	1.458	1.458	1.445	---	---	---
C3-C6	---	---	---	---	1.473	1.471	1.472
C6-O	1.230	1.225	1.232	1.227	1.225	1.220	1.227
C6-C7	1.518	1.513	1.508	1.500	1.521	1.516	1.511
C2-N-C5	110.2	110.1	110.3	109.5	110.1	110.1	110.5
N-C2-C6	118.6	119.5	119.5	121.6	---	---	---
C2-C3-C6	---	---	---	---	123.5	123.8	124.0
N-C5-C4	108.0	108.1	107.7	108.4	107.6	107.6	107.5
N-C2-C3	107.0	107.1	107.3	107.0	107.9	107.9	107.4
C3-C4-C5	107.2	107.2	107.4	107.4	107.5	107.5	107.4
C2-C3-C4	107.6	107.6	107.3	107.6	106.8	106.8	107.3
C2-C6-C7	118.1	118.2	117.4	118.2	---	---	---
C3-C6-C7	---	---	---	---	117.6	117.7	117.0
C3-C2-C6	134.3	133.5	133.3	131.4	---	---	---
C4-C3-C6	---	---	---	---	129.7	129.4	129.4
C2-C6-O	120.1	120.2	120.4	121.6	---	---	---
C3-C6-O	---	---	---	---	121.4	121.4	121.5
C5-N-H	128.4	127.7	127.7	123.0	125.0	125.0	124.8

[a] Distances are in Å and angles in degrees.

[b] Camarillo, E. A.; Flores, H.; Amador P.; Bernès S. *Acta Cryst*. **2007**, *E63*, o2593-o2594.

Table S5

G3(MP2)//B3LYP computed enthalpies (energies plus thermal corrections for *T*=298.15 K) for the 2- and 3-acetylpyrroles and for the auxiliary molecules and atoms used in the gas-phase working reactions.[a]

	Computed G3(MP2)//B3LYP Enthalpies
2-acetylpyrrole (syn)	**–362.268339**
2-acetylpyrrole (anti)	–362.261766
3-acetylpyrrole (syn)	**–362.262702**
3-acetylpyrrole (anti)	–362.262414
2-acetylthiophene (syn)	**–704.743889**
2-acetylthiophene (anti)	–704.742911
3-acetylthiophene (syn)	–704.742241
3-acetylthiophene (anti)	**–704.742881**
pyrrole	–209.822528
thiophene	–552.305094
benzene	–231.835149
acetophenone	–384.271868
water	–76.34187
ethane	–79.651016
methena	–40.420546
acetic acid	–228.786556
propanone	–192.847394
2-methylpyrrole	–249.062717
3-methylpyrrole	–249.060687
hydrogen	–0.499780
carbon	–37.788425
nitrogen	–54.524582
oxygen	–74.989704

[a] Values in bold correspond to the most stable configurations; all energies are in Hartrees (1 Hartree = 2625.5 kJ·mol^{-1})

Table S6

Standard molar enthalpies of formation, at T = 298.15 K, taken from the literature

Compound	$\frac{\Delta_f H_m^o(g)}{kJ \cdot mol^{-1}}$
2-acetylthiophene	−59.2 ± 2.1 [a]
3-acetylthiophene	−54.5 ± 1.8 [a]
pyrrole	108.4 ± 0.6 [b]
thiophene	115.0 ± 1.0 [c]
benzene	82.6 ± 0.7 [b]
acetophenone	−86.7 ± 1.5 [b]
water	−241.826 ± 0.040 [d]
etano	−83.8 ± 0.3 [b]
methane	−74.4 ± 0.4 [b]
acetic acid	−432.8 ± 2.5 [b]
propanone	−217.1 ± 0.7 [b]
2-methylpyrrole	74.91[e]
3-metylpyrrole	80.24[e]
furan	−34.8 ± 0.7 [b]
2-furanocarboxylic acid	−410.3 ± 2.1 [f]
3-furanocarboylic acid	−415.8 ± 1.7 [f]
2-acetylfuran	−207.4 ± 1.3 [g]
3-acetylfuran	−205.04[e]
hydrogen	218.00 [h]
carbon	716.67 [h]
nitrogen	472.68 [h]
oxygen	249.17 [h]

[a] Roux, M. V.; Temprado, M.; Jiménez, P.; Notário, R.; Chickos, J. S.; Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V., *J. Phys. Chem. A*, **2007**, *111*, 11084-11092.

[b] Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*, Thermodynamics Research Centre, College Station, TX, **1994**.

[c] Hubbard, W. N.; Scott, D. W.; Frow, F. R.; Waddington, G., *J. Am. Chem. Soc.* **1955,** *77***,** 5855-5858.

[d] Cox, J. D.; Wagman, D. D.; Medvedev, V. A., Eds. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

[e] Estimated by the G3MP2B3 method, through the respective atomization reaction.

[f] Roux, M. V.; Temprado, M.; Jiménez, P.; Pérez-Parajón, J.; Notário, R., *J. Phys. Chem. A*, **2003**, *107*, 11460-11467.

[g] Unpublished results

[h] Chase, M.W., Jr.,*J. Phys. Chem. Ref. Data* **1998**, Monograph 9, 1-1951.

Table S7

Comparison between the experimental and computed B3LYP/6-311+G(2d,2p) and MP2 / 6311+G(2d,2p) gas-phase enthalpies of formation of 2- and 3-acetylpyrroles, at $T = 298.15$ K [a]

	2-acetylpyrrole		**3-acetilpirrole**	
	$-\Delta_f H_m^o(g)$ / kJ·mol^{-1}		$-\Delta_f H_m^o(g)$ / kJ·mol^{-1}	
Reaction	B3LYP/ 6311+G(2d,2p)	MP2/ 6311+G(2d,2p)	B3LYP/ 6311+G(2d,2p)	MP2/ 6311+G(2d,2p)
(7)	88.4 (7.0)	83.6 (2.2)	69.4 (4.4)	65.9 (0.9)
(8)	92.4 (11.0)	87.3 (5.9)	74.3 (9.3)	69.3 (4.3)
(9)	77.5 (−3.9)	98.8 (17.4)	59.4 (−5.6)	80.0 (15.8)
(10)	83.6 (2.2)	93.7 (12.3)	65.5 (0.5)	75.8 (10.8)
(11)		88.6 (7.2)		70.2 (5.2)
(12)		82.2 (0.8)		68.6 (3.6)

[a] Enthalpic differences between the experimental and computed values are given in parentheses. All values are in kJ·mol^{-1}

Table S8

G3(MP2)//B3LYP computed proton affinities, PA, at $T = 298.15$ K for pyrrole and for the 2- and 3-acetylpyrroles. Values are in $kJ \cdot mol^{-1}$.

Protonation site	Pyrrole	2-acetylpyrrole	3-acetylpyrrole
N	798.2 797 [a]	786.3	772.2
C2	**872.9** **874** [a]	831.7	852.2
C3	854.3 855 [a]	822.9	820.2
C4	---	836.8	833.4
C5	---	839.6	853.4
O	---	**892.9**	**900.6**

[a] Kabli, S.; van Beelen, E. S. E.; Ingemann, S.; Henriksen, L.; Hammerum, S. *Int. J. Mass Spectrom.* **2006**, *249-150*, 370-378.