SUPPLEMENTARY INFORMATION

Energetic effects in methyl- and methoxy-substituted indanones: a synergistic experimental and computational study

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This supplementary information includes:

- the data of all the combustion calorimetry experiments of indanones (**Tables S1-S4**);
- the corresponding values of standard molar heat capacities in the gaseous phase (**Table S5**)
- the areas and transmission probability factors of the effusion orifices (**Table S6**) and the data of all the effusion experiments for 5-methoxy-1-indanone (**Table S7**);
- the molecular structures of the most stable conformation of 2-methyl-1-indanone, 3-methyl-1-indanone and 4-methoxy-1-indanone in the gaseous phase, optimized by B3LYP/6-31G(d) level of theory (**Fig. S1**);
- the conformational analysis of 5-methoxy-1-indanone (**Table S8**);
- the working reactions for the estimation of the gas-phase enthalpy of formation of indanones (Tables S9-S12) and for 2-methylcyclopentanone (**Table S13**);
- G3(MP2)//B3LYP calculated absolute enthalpies, at T = 298.15 K, and experimental gas-phase values for all the molecules used (**Table S14**).

Acronyms used throughout this supplementary data:

2MI for 2-methyl-1-indanone

3MI for 3-methyl-1-indanone

4MI for 4-methoxy-1-indanone

5MI for 5-methoxy-1-indanone

SECTION 1 - Combustion Calorimetry

- The calibration of the calorimeters was performed by combustion of benzoic acid (NIST SRM 39j), whose massic energy of combustion, under bomb conditions, is –(26434 ± 3) $J \cdot g^{-1}$;
  - Calorimetric system I – two values of the energy equivalent of the calorimeter, ε_{cal} = (15546.7 ± 1.6) $J \cdot K^{-1}$, and ε_{cal} = (15553.0 ± 1.1) $J \cdot K^{-1}$, were obtained (on two separate occasions) and refer to an average mass of 2900.0 g of water added to the calorimeter;
  - Calorimetric system II – the energy equivalent of the calorimeter, ε_{cal} = (16002.6 ± 1.7) $J \cdot K^{-1}$, was obtained and corresponds to the average mass of water added to the calorimeter (3119.6 g);
    The uncertainties quoted are the standard deviation of the mean of six calibration experiments.
    Some experiments of **2MI** and **4MI** were performed with the combustion calorimetric system II due to an unexpected problem in one of the valves of the bomb.
- Liquid samples of **2MI and 3MI** were burnt enclosed into Melinex bags, under oxygen at p = 3.04 MPa, with 1.00 cm^3 of deionised water added to the bomb;
- Solids samples of **4MI** and **5MI** were ignited in pellet form and under the same condition mentioned above;
- n-Hexadecane (Aldrich, mass fraction > 0.999), stored under nitrogen, was added to each pellet of **4MI** to prevent incomplete combustions; the massic energy of combustion of the sample used, was determined in our laboratory as $\Delta_c u^\circ$ = –(47136.7 ± 2.3) $J \cdot g^{-1}$;
- Melinex bags were made according to the technique described by Skinner et al. [S1]; the massic energy of combustion of dry Melinex and respective expanded uncertainty was –(22902 ± 5) $J \cdot g^{-1}$;
- The cotton thread fuse (empirical formula: $CH_{1.686}O_{0.843}$) had a standard massic energy of combustion [S2], $\Delta_c u^\circ$ = –16240 $J \cdot g^{-1}$;
- The ignition energy was determined from the change in potential difference on discharge of a 1400 μF condenser across a platinum wire;
- Pressure coefficient of specific energy $(\partial u/\partial p)_T$ = –0.2 $J \cdot g^{-1} \cdot MPa^{-1}$ (typical value for organic compounds [S3]);
- The energetic correction for the nitric acid formation, $\Delta U(HNO_3)$ was based on –59.7 $kJ \cdot mol^{-1}$ for the molar energy of formation of 0.1 $mol \cdot dm^{-3}$ HNO_3(aq) from N_2(g), O_2(g), and H_2O(l);
- Corrections for carbon formation relied on the standard massic energy of combustion of carbon [S4], $\Delta_c u^\circ$ = –32.76 $kJ \cdot g^{-1}$;
- Specific density of the studied compounds and auxiliaries, at T = 298.15 K:
  ρ = 1.064 $g \cdot cm^{-3}$ for **2MI** [S5], ρ = 1.075 $g \cdot cm^{-3}$ for **3MI** [S5], ρ = 1.0799 $g \cdot cm^{-3}$ for **4MI**, ρ = 1.292 $g \cdot cm^{-3}$ **5MI** [S6], ρ = 1.38 $g \cdot cm^{-3}$ for Melinex [S1] and ρ = 1.50 $g \cdot cm^{-3}$ for cotton fuse [S7];
- The values of the massic heat capacities, at T = 298.15 K, were calculated as 1.634 $J \cdot K^{-1} g^{-1}$ for **2MI** and **3MI** and 1.303 $J \cdot K^{-1} g^{-1}$ for **4MI** and **5MI**, using Kopp's rule [S8].

Table S1 Standard (p^o = 0.1 MPa) mass energy of combustion of liquid 2-methyl-1-indanone (**2MI**), at T = 298.15 K.

	1	2	3	4*	5*	6*
m(cpd)/g	0.37494	0.38190	0.43874	0.40037	0.44589	0.42273
m(fuse)/g	0.00286	0.00244	0.00217	0.00252	0.00249	0.00261
m(melinex)/g	0.05215	0.05616	0.05573	0.05467	0.05434	0.05432
T_i/K	298.1510	298.1513	298.1515	298.1505	298.1505	298.1515
T_f/K	299.1669	299.1886	299.3147	299.2016	299.2995	299.2493
ΔT_{ad}/K	0.93608	0.95723	1.08524	0.96877	1.06939	1.01773
ε_i/J·K^{-1}	14.10	14.10	14.12	15.87	15.88	15.87
ε_f/J·K^{-1}	15.11	15.14	15.31	16.95	17.09	17.02
$(\varepsilon_{cal})_{corr}$/J·K^{-1}	15541.68	15537.91	15543.77	—	—	—
$\Delta m(H_2O)$/g	−1.2	−2.1	−0.7	0.0	0.0	0.0
$-\Delta U$(IBP)/J	14561.80	14887.29	16884.84	15518.76	17130.38	16302.77
$\Delta U(HNO_3)$/J	1.03	1.36	1.99	1.95	1.27	1.20
ΔU(ign)/J	0.60	0.56	0.50	0.50	0.91	0.88
ΔU_Σ/J	8.12	8.35	9.54	8.64	9.58	9.09
$-\Delta U$(melinex)/J	1194.32	1286.16	1276.34	1252.12	1244.58	1244.12
$-\Delta U$(fuse)/J	46.45	39.63	35.24	40.92	40.44	42.39
$-\Delta_c u^o$/(J·g^{-1})	35504.03	35485.18	35469.14	35504.96	35512.14	35499.74
% CO_2 = (99.93 ± 0.07) [a]						
$\langle\Delta_c u^\circ\rangle$ = −(35495.53 ± 6.44) J·g^{-1} [a]						

m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(melinex) is the mass of melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalents of contents in the initial and final state; $(\varepsilon_{cal})_{corr}$ is the corrected energy equivalent of the calorimeter I for the amount of water used in the calorimeter (exp. 1 to 3), for this calculation ε_{cal} = (15546.7 ± 1.6) J·K^{-1} was used; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 2900.0 g (exp. 1 to 3; calorimetric system I) and 3119.6 g (exp. 4 to 6; calorimetric system II); ΔU(IBP) is the energy change for the isothermal combustion reaction and includes ΔU(ign); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; ΔU(melinex) is the energy of combustion of the melinex; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion.
*Energy equivalent of the calorimeter II, ε_{cal} = (16002.6 ± 1.7) J·K^{-1}, was used. [a] Mean value and standard deviation of the mean.

Table S2 Standard (p^o = 0.1 MPa) mass energy of combustion of liquid 3-methyl-1-indanone (**3MI**), at T = 298.15 K.

	1	2	3	4	5	6
m(cpd)/g	0.38534	0.49432	0.46788	0.39851	0.37742	0.35060
m(fuse)/g	0.00329	0.00277	0.00279	0.00250	0.00224	0.00281
m(melinex)/g	0.04789	0.05589	0.05532	0.04241	0.05394	0.05647
T_i/K	298.1504	298.1511	298.1506	298.1508	298.1509	298.1504
T_f/K	299.1866	299.4402	299.3816	299.2088	299.1756	299.1189
ΔT_{ad}/K	0.95602	1.21731	1.15597	0.97730	0.94498	0.88771
ε_i/J·K^{-1}	13.20	13.20	13.19	13.15	13.16	13.16
ε_f/J·K^{-1}	14.20	14.50	14.42	14.19	14.15	14.07
$(\varepsilon_{cal})_{corr}$/J·K^{-1}	15543.35	15540.42	15538.33	15550.05	15553.00	15551.33
$\Delta m(H_2O)$/g	−0.8	−1.5	−2.0	0.8	0.0	−0.4
$-\Delta U$(IBP)/J	14872.72	18934.39	17977.75	15210.21	14710.03	13816.98
$\Delta U(HNO_3)$/J	2.44	1.34	0.97	0.79	1.33	2.67
ΔU(ign)/J	0.61	0.77	0.76	0.72	0.61	0.58
ΔU_Σ/J	8.34	10.86	10.27	8.48	8.25	7.79
$-\Delta U$(melinex)/J	1096.78	1279.99	1266.97	971.36	1235.44	1293.24
$-\Delta U$(fuse)/J	53.43	44.98	45.31	40.60	36.38	45.63
$-\Delta_c u^o$/(J·g^{-1})	35583.46	35598.84	35595.09	35605.08	35580.10	35560.90
% CO_2 = (99.28 ± 0.07) [a]						
$\langle\Delta_c u^\circ\rangle$ = −(35587.25 ± 6.52) J·g^{-1} [a]						

m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(melinex) is the mass of melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalents of contents in the initial and final state; $(\varepsilon_{cal})_{corr}$ is the corrected energy equivalent of the calorimeter for the amount of water used in the calorimeter, for this calculation, ε_{cal} = (15546.7 ± 1.6) J·K^{-1} was used, except in exps. 5 and 6, in which ε_{cal} = (15553.0 ± 1.1) J·K^{-1}; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 2900.0 g; ΔU(IBP) is the energy change for the isothermal combustion reaction and includes ΔU(ign); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; ΔU(melinex) is the energy of combustion of the melinex; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion.

[a] Mean value and standard deviation of the mean.

Table S3 Standard (p^o = 0.1 MPa) mass energy of combustion of solid 4-methoxy-1-indanone (**4MI**), at T = 298.15 K.

	1	2	3	4	5*	6*
m(cpd)/g	0.49212	0.47396	0.35075	0.41472	0.42282	0.42886
m(fuse)/g	0.00229	0.00236	0.00272	0.00205	0.00252	0.00240
m(n-hexadec.)/g	0.10431	0.06766	0.10944	0.09710	0.10640	0.10468
T_i/K	298.1504	298.1514	298.1548	298.1504	298.1508	298.1511
T_f/K	299.5198	299.3785	299.2680	299.3503	299.3637	299.3734
ΔT_{ad}/K	1.30199	1.15408	1.03565	1.12577	1.13700	1.14400
ε_i/J·K^{-1}	13.80	13.70	13.64	13.69	15.03	15.03
ε_f/J·K^{-1}	14.83	14.57	14.48	14.59	15.96	15.97
$(\varepsilon_{cal})_{corr}$/J·K^{-1}	15559.28	15558.02	15549.65	15553.00	—	—
Δm(H_2O)/g	1.5	1.2	−0.8	0.0	0.0	0.0
$-\Delta U$(IBP)/J	20276.64	17971.46	16118.42	17524.96	18212.62	18324.77
ΔU(HNO_3)/J	0.60	1.40	0.64	0.63	0.69	0.65
ΔU(ign)/J	0.70	0.56	0.58	0.57	0.72	0.72
ΔU_Σ/J	10.56	9.65	7.70	8.84	9.03	9.13
ΔU(carb)/J	—	5.94	—	—	—	—
$-\Delta U$(n-hexadec.)/J	4916.79	3189.45	5158.43	4576.99	5015.43	4934.25
$-\Delta U$(fuse)/J	37.19	38.33	44.17	33.29	40.92	38.98
$-\Delta_c u^o$/(J·g^{-1})	31113.35	31096.65	31097.59	31117.89	31091.95	31109.22
% CO_2 = (100.04 ± 0.02) [a]						
$\langle\Delta_c u^\circ\rangle$ = −(31104.44 ± 4.27) J·g^{-1} [a]						

m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(n-hexadec.) is the mass of n-hexadecane used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalents of contents in the initial and final state; $(\varepsilon_{cal})_{corr}$ is the corrected energy equivalent of the calorimeter I for the amount of water used in the calorimeter (exp. 1 to 4), for this calculation ε_{cal} = (15553.0 ± 1.1) J·K^{-1} was used; Δm(H_2O) is the deviation of the mass of water added to the calorimeter from 2900.0 g (exp. 1 to 4; calorimetric system I) and 3119.6 g (exp. 5 and 6; calorimetric system II); ΔU(IBP) is the energy change for the isothermal combustion reaction and includes ΔU(ign); ΔU(HNO_3) is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; ΔU(carb.) is the correction energy for carbon soot formation; ΔU(n-hexadec.) is the energy of combustion of the n-hexadecane; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion.*Energy equivalent of the calorimeter, ε_{cal} = (16002.6 ± 1.7) J·K^{-1}, was used. [a] Mean value and standard deviation of the mean.

Table S4 Standard (p^o = 0.1 MPa) mass energy of combustion of solid 5-methoxy-1-indanone (**5MI**), at T = 298.15 K.

	1	2	3	4	5	6
m(cpd)/g	0.59158	0.61595	0.61366	0.60916	0.61473	0.61148
m(fuse)/g	0.00299	0.00289	0.00285	0.00294	0.00282	0.00290
T_i/K	298.1512	298.1506	298.1504	298.1508	298.1509	298.1511
T_f/K	299.3831	299.4235	299.4187	299.4124	299.4208	299.4154
ΔT_{ad}/K	1.15181	1.19865	1.19449	1.18615	1.19537	1.19056
ε_i /J·K^{-1}	16.14	16.17	16.17	16.16	16.17	16.16
ε_f /J·K^{-1}	16.99	17.06	17.05	17.04	17.05	17.05
$-\Delta U$(IBP)/J	18450.89	19201.31	19134.71	19000.88	19148.57	19071.34
$\Delta U(HNO_3)$/J	0.52	0.48	0.65	0.62	0.48	0.41
ΔU(ign) /J	0.62	0.64	0.59	0.80	0.83	0.91
ΔU_Σ /J	11.01	11.52	11.47	11.38	11.48	11.43
ΔU(carb)/J	2.64	5.94	11.55	3.96	26.40	6.60
$-\Delta U$(fuse) /J	48.56	46.93	46.28	47.75	45.80	47.10
$-\Delta_c u^o$ /(J·g^{-1})	31092.06	31087.46	31104.94	31100.35	31098.55	31103.37

% CO_2 = (99.99 ± 0.04) [a]

$<\Delta_c u^\circ>$ = −(31097.79 ± 2.76) J·g^{-1} [a]

m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(carb) is the mass of carbon; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalents of contents in the initial and final state; ΔU(IBP) is the energy change for the isothermal combustion reaction and includes ΔU(ign), for this calculation, ε_{cal} = (16002.6 ± 1.7) J·K^{-1} was used; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; ΔU(carb.) is the correction energy for carbon soot formation; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion. [a] Mean value and standard deviation of the mean.

SECTION 2 – Calvet microcalorimetry

Samples of ~5 mg were dropped, simultaneously with the corresponding blank tube, at room temperature (T ~ 298 K), into the reaction vessel of the microcalorimeter (at a pre-defined temperature). After the tubes reached thermal equilibrium, the sample was removed from the hot-zone by sublimation or vaporization under reduced pressure. A correction, k, to the internal calibration constant of the calorimeter was obtained as the average of six independent experiments with naphthalene (Sigma-Aldrich 99.9%), k = (1.038 ± 0.003) at T = 366 K for 4MI and 5MI. Undecane (Sigma-Aldrich 99.9%) was used in the calibration study for liquids: k = (1.039 ± 0.008) at T = 345 K for 2MI and k = (1.027 ± 0.008) at T = 355 K for 3MI.

TABLE S5
Standard (p^o = 0.1 MPa) molar heat capacities in the gaseous phase for the studied compounds.

T / K	$\frac{C^o_{p,m}(g)}{J\cdot K^{-1}\cdot mol^{-1}}$	T / K	$\frac{C^o_{p,m}(g)}{J\cdot K^{-1}\cdot mol^{-1}}$
2MI		**3MI**	
150	87.83	150	87.22
200	111.41	200	111.08
250	137.08	250	137.01
298.15	162.80	298.15	162.88
300	163.79	300	163.88
350	190.17	350	190.33
400	215.17	400	215.35
450	238.22	450	238.40
500	259.15	500	259.30
550	278.02	550	278.15
4MI		**5MI**	
150	100.18	150	99.79
200	125.17	200	124.97
250	151.78	250	151.74
298.15	178.17	298.15	178.22
300	179.18	300	179.24
350	206.18	350	206.28
400	231.79	400	231.92
450	255.46	450	255.61
500	277.01	500	277.15
550	296.47	550	296.61

$$C^{\circ}_{p,m}(\text{2MI, g})/\left(J\cdot K^{-1}\cdot mol^{-1}\right) = -9.950\times10^{-7}\,T^3 + 8.663\times10^{-4}\,T^2 + 2.744\times10^{-1}\,T + 30.23$$

$$C^{\circ}_{p,m}(\text{3MI, g})/\left(J\cdot K^{-1}\cdot mol^{-1}\right) = -9.747\times10^{-7}\,T^3 + 8.348\times10^{-4}\,T^2 + 2.901\times10^{-1}\,T + 27.90$$

$$C^{\circ}_{p,m}(\text{4MI, g})/\left(J\cdot K^{-1}\cdot mol^{-1}\right) = -9.122\times10^{-7}\,T^3 + 7.639\times10^{-4}\,T^2 + 3.276\times10^{-1}\,T + 36.70$$

$$C^{\circ}_{p,m}(\text{5MI, g})/\left(J\cdot K^{-1}\cdot mol^{-1}\right) = -8.990\times10^{-7}\,T^3 + 7.442\times10^{-4}\,T^2 + 3.373\times10^{-1}\,T + 35.24$$

SECTION 3 – Knudsen effusion method

- The apparatus is prepared for the simultaneous use of nine effusion cells grouped in three series ("Small" – series A; "Medium" – series B; "Large" – series C);
- The areas and transmission probability factors of the effusion orifices are presented in Table S6;
- The temperature of each block is measured by a platinum resistance thermometer Pt-100 class 1/10;
- For the temperature *T*, the vapour pressure *p* of the crystalline compound is related to the mass *m* of the sample sublimed from each effusion cell, during the time period *t* by equation (S1), where *M* is the molar mass of the effusing vapour, *R* is the gas constant, A_0 is the area of the effusion orifice and w_0 is the respective transmission probability factor (calculated using the equation presented in Table S6).

$$p = (m/A_0 w_0 t)\cdot(2\pi R T/M)^{1/2} \quad \text{(S1)}$$

Table S6. Area and transmission probability factors of the effusion orifices

	Orifice	A_o/mm^2	w_o
Series A	A_1	0.502	0.988
	A_2	0.509	0.988
	A_3	0.503	0.988
Series B	B_4	0.774	0.991
	B_5	0.783	0.991
	B_6	0.792	0.991
Series C	C_7	1.099	0.992
	C_8	1.125	0.992
	C_9	1.131	0.992

$w_o=\{1+(3l/8r)\}^{-1}$, where l is the length of the effusion orifice (l = 0.0125 mm) and r is its radius.

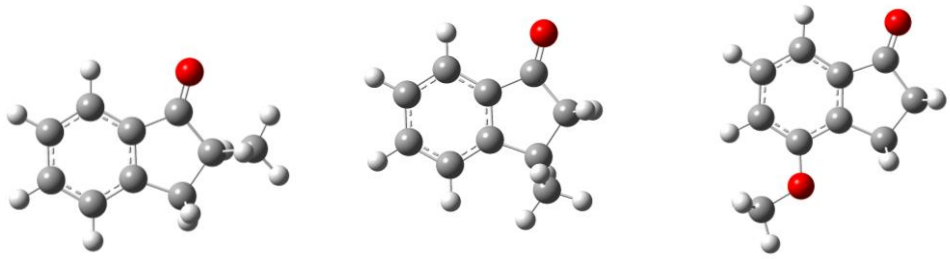
Table S7. Effusion results for 5MI in solid phase

T^a / K	t / s	Orifices	m / mg			p^b / Pa		
			m_A	m_B	m_C	p_A	p_B	p_C
315.397	23448	A_3-B_6-C_9	4.53	5.53	6.99	0.098	0.097	0.098
317.307	23448	A_2-B_5-C_8	5.68	7.00	8.75	0.123	0.123	0.122
319.091	23448	A_1-B_4-C_7	7.06	8.94	10.88	0.154	0.158	0.153
321.279	27214	A_2-B_5-C_8	10.52	12.93	16.26	0.198	0.197	0.197
323.096	27214	A_1-B_4-C_7	13.08	16.54	20.02	0.247	0.253	0.244
325.524	16320	A_3-B_6-C_9	9.80	12.00	15.25	0.310	0.307	0.311
327.280	16320	A_2-B_5-C_8	12.18	15.04	18.83	0.386	0.386	0.384
329.088	16320	A_1-B_4-C_7	15.08	19.15	22.98	0.480	0.492	0.470
331.390	11514	A_3-B_6-C_9	13.70	16.63	21.10	0.620	0.608	0.614
333.305	11514	A_2-B_5-C_8	16.81	20.76	25.79	0.762	0.762	0.753
335.093	11514	A_1-B_4-C_7	20.71	26.20	31.62	0.942	0.964	0.926
337.323	10969	A_3-B_6-C_9	25.14	30.36	38.83	1.204	1.176	1.198

[a] The standard uncertainty of the temperature is $u(T) = \pm 0.01$ K.

[b] The standard uncertainty of the pressure is $u(p) = \pm 0.05$ Pa.

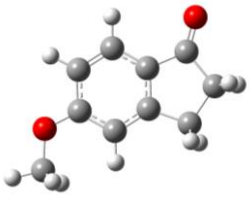
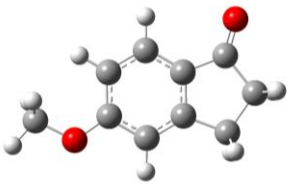
SECTION 4 – Computational study



2MI **3MI** **4MI**

Fig. S1. Molecular structures of the most stable conformation of 2MI, 3MI and 4MI in the gaseous phase, optimized by B3LYP/6-31G(d) level of theory.

Table S8. Conformational analysis of 5MI, corresponding total electronic energy plus the internal thermal energy, $E^{\circ}_{298.15\ K}$, and G3(MP2)//B3LYP results for both conformers

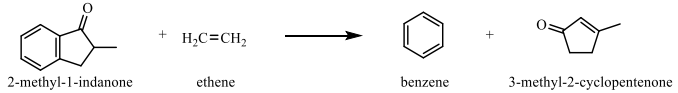
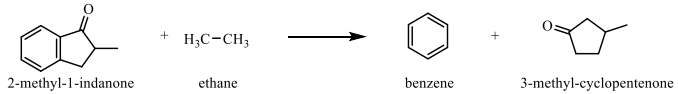
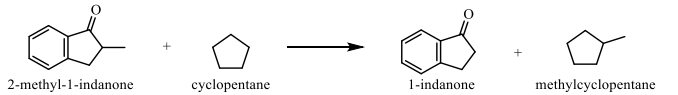
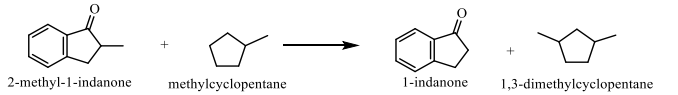
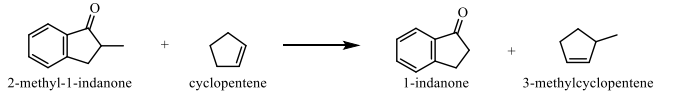
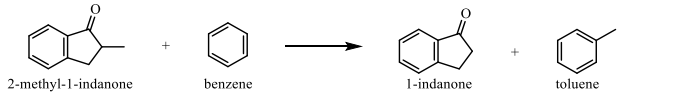
Conformer	$E^{\circ}_{298.15\ K}$ [a]	H°_{m} [a]	G°_{m} [a]	$\Delta G_{rel}(i)$ [b]	χ_i [c]
 I	-536.698137	-536.697193	-536.744919	0.00	59.55
 II	-536.697679	-536.696735	-536.744554	0.96	40.45
Weighted value of H°_{m} = -536.697008 hartrees used in the calculations					

[a] In Hartrees: 1 Hartree = 2625.5 kJ·mol^{-1};

[b] Value calculated according to this formula: $\Delta G_{rel}(i) = G^{\circ}_{m}(i) - G^{\circ}_{m}$(conformer I); in kJ·mol^{-1};

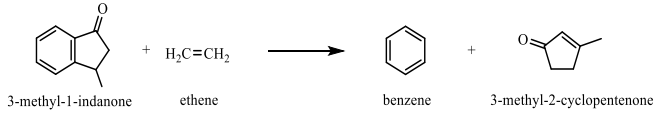
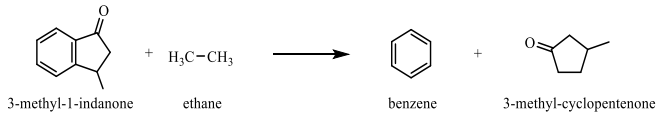
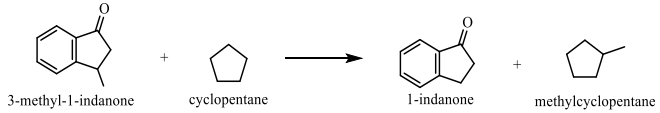
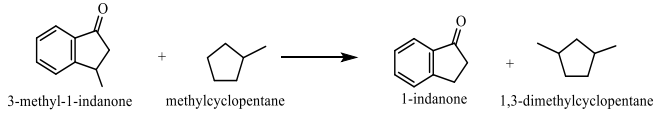
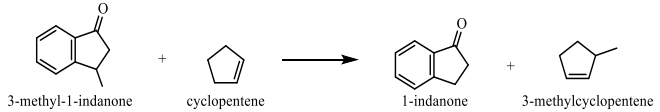
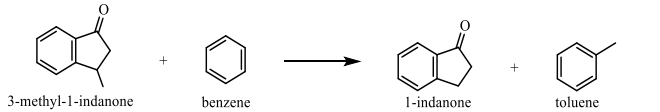
[c] Value calculated using the formula: $\chi_i = \frac{e^{-\frac{\Delta G_{rel}(i)}{RT}}}{\sum_{i=1}^{n} e^{-\frac{\Delta G_{rel}(i)}{RT}}}$.

Table S9. Working reactions for **2MI** and corresponding values for the enthalpies of reaction and formation in the gaseous-phase, at T = 298.15 K (values in kJ·mol^{-1}). [a]

Working reactions		$\Delta_r H^\circ_m$(g)	$\Delta_f H^\circ_m$(calc., g)
	(1)	-11.62	-101.7
	(2)	34.07	-96.0
	(3)	-1.10	-92.7
	(4)	0.32	-91.7
	(5)	0.20	-90.8
	(6)	-2.89	-93.6
		$\langle\Delta_f H^\circ_m$(calc., g)$\rangle = -(94.4 \pm 4.2)$ kJ·mol^{-1}	

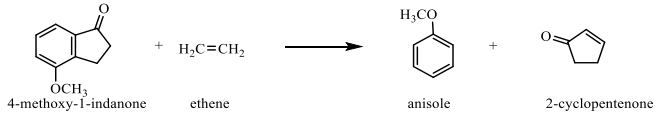
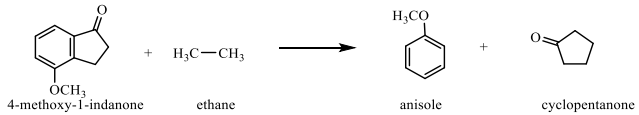
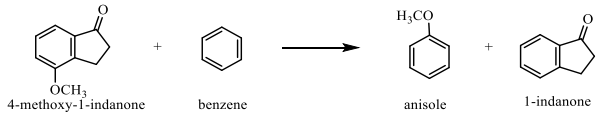
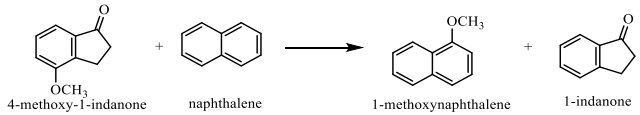
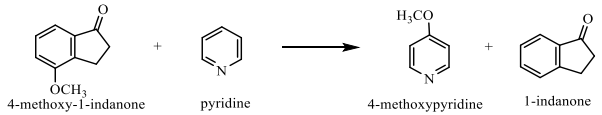
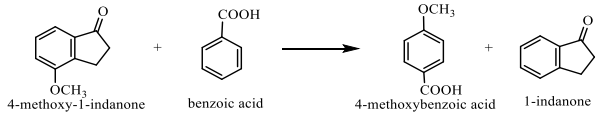
[a] The corresponding assigned uncertainty is twice the standard error of the mean of six results.

Table S10. Working reactions for **3MI** and corresponding values for the enthalpies of reaction and formation in the gaseous-phase, at T = 298.15 K (values in kJ·mol^{-1}). [a]

Working reactions		$\Delta_r H^\circ_m$(g)	$\Delta_f H^\circ_m$(calc., g)
	(1)	-11.71	-101.6
	(2)	33.97	-95.9
	(3)	-1.20	-92.6
	(4)	0.23	-91.6
	(5)	0.11	-90.7
	(6)	-2.99	-93.5
		$\langle\Delta_f H^\circ_m$(calc., g)$\rangle$ = –(94.3 ± 4.2) kJ·mol^{-1}	

[a] The corresponding assigned uncertainty is twice the standard error of the mean of six results.

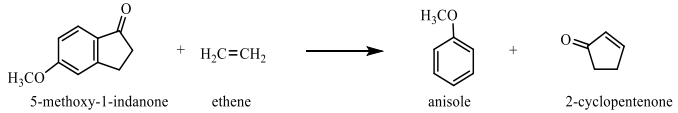
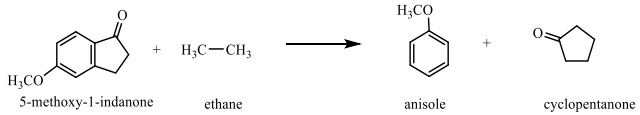
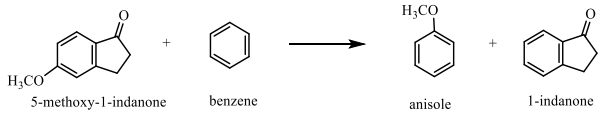
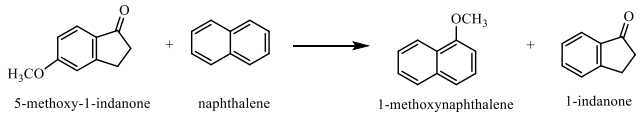
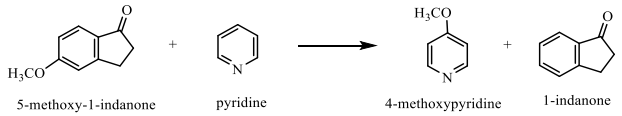
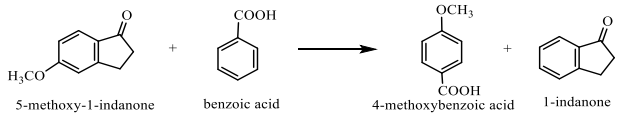
Table S11. Working reactions for **4MI** and corresponding values for the enthalpies of reaction and formation in the gaseous-phase, at T = 298.15 K (values in kJ·mol^{-1}). [a]

Working reactions		$\Delta_r H^\circ_m$(g)	$\Delta_f H^\circ_m$(calc., g)
	(1)	6.19	-224.7
	(2)	39.35	-215.5
	(3)	3.30	-217.8
	(4)	0.92	-218.2
	(5)	-4.62	-218.0
	(6)	-1.36	-220.5

$<\Delta_f H^\circ_m(\text{calc., g})> = -(219.1 \pm 3.3)$ kJ·mol^{-1}

[a] The corresponding assigned uncertainty is twice the standard error of the mean of six results.

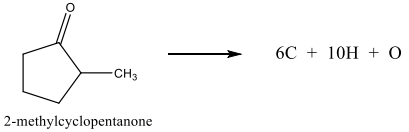
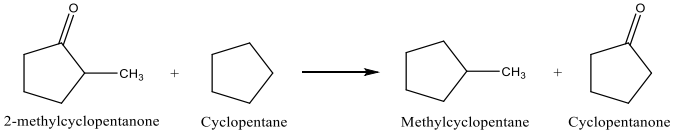
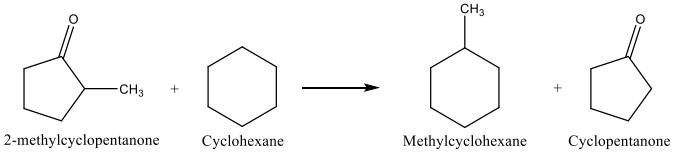
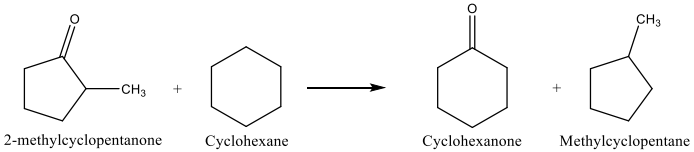
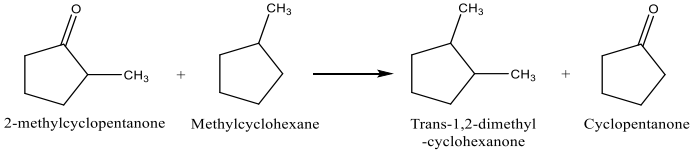
Table S12. Working reactions for **5MI** and corresponding values for the enthalpies of reaction and formation in the gaseous-phase, at T = 298.15 K (values in kJ·mol^{-1}). [a]

Working reactions		$\Delta_r H^\circ_m$(g)	$\Delta_f H^\circ_m$(calc., g)
	(1)	7.33	-225.8
	(2)	40.49	-216.7
	(3)	4.45	-219.0
	(4)	2.07	-219.4
	(5)	-3.47	-219.1
	(6)	-0.21	-221.7

$<\Delta_f H^\circ_m(\text{calc., g})> = -(220.3 \pm 3.3)$ kJ·mol^{-1}

[a] The corresponding assigned uncertainty is twice the standard error of the mean of six results.

Table S13. Working reactions for 2-methylcyclopentanone and corresponding values for the enthalpies of reaction and formation in the gaseous-phase, at T = 298.15 K (values in kJ·mol^{-1}). [a]

Working reactions		$\Delta_r H^\circ_m$(g)	$\Delta_f H^\circ_m$(calc., g)
 2-methylcyclopentanone	(1)	6952.47	-223.3
 2-methylcyclopentanone + Cyclopentane → Methylcyclopentane + Cyclopentanone	(2)	0.39	-227.6
 2-methylcyclopentanone + Cyclohexane → Methylcyclohexane + Cyclopentanone	(3)	-0.70	-228.0
 2-methylcyclopentanone + Cyclohexane → Cyclohexanone + Methylcyclopentane	(4)	13.33	-227.3
 2-methylcyclopentanone + Methylcyclohexane → Trans-1,2-dimethyl-cyclohexanone + Cyclopentanone	(5)	-0.55	-227.3
		$\langle\Delta_f H^\circ_m$(calc., g)$\rangle = -(226.7 \pm 2.4)$ kJ·mol^{-1}	

[a] The corresponding assigned uncertainty is twice the standard error of the mean of five results.

Table S14. G3(MP2)//B3LYP absolute enthalpies (in *Hartrees**) and experimental enthalpies of formation (in kJ·mol^{-1}), in the gaseous state, at T = 298.15, for the studied compounds and the auxiliary molecules used in the gas-phase working reactions.

auxiliary molecules	G3(MP2)//B3LYP absolute enthalpies	Experimental enthalpies of formation (298.15 K)
2-methyl-1-indanone (2MI)	-461.563388	(-105.4 ± 3.4) [a]
3-methyl-1-indanone (3MI)	-461.563351	(-92.9 ± 3.3) [a]
4-methoxy-1-indanone (4MI)	-536.696571	(-217.6 ± 3.4) [a]
5-methoxy-1-indanone (5MI)	-536.697008	(-215.6 ± 2.0) [a]
1,3-dimethylcyclopentane	-274.639267	(-133.6 ± 1.4) [S9]
1-indanone	-422.325250	(-64.0 ± 3.8) [S10]
1-methoxynaphthalene	-499.594649	(-3.0 ± 3.1) [S11]
2-cyclopentenone	-268.923985	(-98.1 ± 3.7) [S12]
2-methylcyclopentanone	-309.366108	(-226.7 ± 2.4) [b]
3-methylcyclopentanone	-309.366295	(-228.3 ± 3.7) [b]
3-methylcyclopentene	-234.194016	(7.4 ± 0.6) [S9]
3-methyl-2-cyclopentenone	-308.167646	(-143.4 ± 2.1) [S12]
4-methoxybenzoic acid	-534.582112	(-451.9 ± 1.4) [S9]
4-methoxypyridine	-362.246513	(-18.2 ± 1.8) [S13]
Anisole	-536.695848	(-216.0 ± 3.1) [S9]
Benzene	-231.835136	(82.6 ± 0.7) [S9]
Benzoic acid	-420.210274	(-294.0 ± 2.2) [S9]
Cyclohexane	-235.407838	(-123.3 ± 0.8) [S9]
Cyclohexanone	-309.367618	(-231.1 ± 0.8) [S9]
Cyclopentane	-196.162695	(-76.4 ± 0.7) [S9]
Cyclopentanone	-270.127404	(-192.1 ± 1.8) [S9]
Cyclopentene	-194.955955	(34.0 ± 1.4) [S9]
Ethane	-79.651018	(-83.8 ± 0.3) [S9]
Ethene	-78.434969	(52.5 ± 0.3) [S9]
Methylcyclohexane	-274.646808	(-154.6 ± 1.0) [S9]
Methylcyclopentane	-235.401252	(-106.2 ± 0.7) [S9]
Naphthalene	-385.223680	(150.3 ± 1.4) [S9]
Pyridine	-247.873423	(140.4 ± 0.7) [S9]
Toluene	-271.074374	(50.1 ± 1.1) [S14]
Trans-1,2-dimethylcyclopentane	-274.640164	(-136.6 ± 1.1) [S9]

[a] This work. [b] Value estimated at the G3(MP2)//B3LYP level of theory. [*] 1 Hartree = 2625.5 kJ·mol^{-1}

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