SUPLEMENTARY INFORMATION

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This supplementary information includes the data (orifices diameters, areas and Clausing factors) of the effusion orifices of the Knudsen effusion apparatus (Table S1), and detailed data of all the Combustion Calorimetry experiments, at T = 298.15 K, for 2-, 3- and 4-chlorobenzophenone and 4,4'-dichlorobenzophenone (respectively, Tables S2, S3, S4 and S5). Finally, computed and estimated enthalpies regarding the mono- and dichlorobenzophenones are given in Table 6.

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

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

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

Table S1. Areas and Clausing factors for the platinum orifices of the Knudsen-effusion apparatus; thickness of the hole: l = 0.0125 mm

Cell	Orifice diameter $2r$/mm	l/r	A_O / mm^2	w_0
A1	0.7998	0.0313	0.502	0.988
A2	0.7974	0.0314	0.499	0.988
A3	0.7952	0.0314	0.497	0.988
B1	0.9924	0.0252	0.774	0.991
B2	0.9986	0.0250	0.783	0.991
B3	0.9920	0.0252	0.773	0.991
C1	1.1920	0.0210	1.116	0.992
C2	1.1970	0.0209	1.125	0.992
C3	1.2098	0.0207	1.150	0.992

Combustion calorimetry results

Tables S2, S3, S4 and S5 register, respectively, the details of all experimental determinations of the standard massic energies of combustion of the compounds studied: 2-, 3- and 4-chlorophenone and 4,4'-dichlorophenone.

The symbols presented in these Tables have the follow meaning:

m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of contents in the initial state; ε_f is the energy equivalent of contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U(As_2O_3)$) is the energy correction for the oxidation of the aqueous solution of As_2O_3 ; ΔU(ign) is the electrical energy for ignition; $\Delta U(H_2PtCl_6)$ is the energy correction for the formation of the platinum complex; ΔU_Σ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion.

[a] ΔU(IBP) includes ΔU(ign)

Table S2 - Standard (p^o = 0.1 MPa) massic energy of combustion of 2-chlorobenzophenone, at T = 298.15 K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.64898	0.73937	0.72246	0.73955	0.74686	0.70927
m'(fuse) / g	0.00267	0.00232	0.00273	0.00263	0.00290	0.00276
ΔT_{ad} / K	0.76116	0.86648	0.84615	0.86582	0.87500	0.83071
ε_i / J·K^{-1}	72.71	72.80	72.68	72.70	72.70	72.67
ε_f / J·K^{-1}	71.77	71.85	71.86	71.90	71.90	71.87
$\Delta m(H_2O)$ / g	-9.3	-6.8	0.4	0.4	-1.4	0.7
$-\Delta U$(IBP)[a] / J	19180.94	21843.94	21356.80	21853.28	22078.40	20968.13
ΔU(fuse) / J	43.36	37.68	44.34	42.71	47.10	44.82
$\Delta U(HNO_3)$ / J	7.76	7.52	12.06	14.21	13.13	14.45
$\Delta U(As_2O_3)$ / J	43.21	57.61	60.62	61.26	62.86	59.34
ΔU(ign.) / J	1.29	1.29	1.29	1.19	1.20	1.29
$\Delta U(H_2PtCl_6)$ / J	0.61	0.97	0.73	0.70	0.69	0.57
$-\Delta U$(carb) / J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	35.60	40.45	35.60	40.51	40.92	38.87
$-\Delta_c u^o$ / J·g^{-1}	29352.38	29347.17	29341.62	29332.97	29339.50	29338.32
$-\langle\Delta_c u^0\rangle$ = (29342.0 ± 2.8) J·g^{-1}						

ε_{cal} = (25165.6 ± 1.5) J·K^{-1}

Table S3 - Standard (p^o = 0.1 MPa) massic energy of combustion of 3-chlorobenzophenone, at T = 298.15 K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.72510	0.74205	0.73286	0.72907	0.71343	0.70310
m'(fuse) / g	0.00280	0.00302	0.00245	0.00284	0.00269	0.00274
ΔT_{ad} / K	0.84653	0.86620	0.85524	0.85123	0.83306	0.82104
ε_i / J·K^{-1}	72.78	72.80	72.79	72.78	72.77	72.66
ε_f / J·K^{-1}	71.79	71.80	71.81	71.81	71.79	71.89
Δm(H_2O) / g	0.8	1.0	-0.2	1.5	0.2	0.4
$-\Delta U$(IBP)[a] / J	21367.89	21865.14	21584.18	21489.03	21025.79	20723.01
ΔU(fuse) / J	45.47	49.04	39.79	46.12	43.69	44.50
ΔU(HNO_3) / J	6.21	7.16	6.57	11.10	11.22	16.72
ΔU(As_2O_3) / J	68.17	73.61	63.69	76.17	74.89	56.46
ΔU(ign.) / J	1.19	1.29	1.29	1.30	1.29	1.29
ΔU(H_2PtCl_6) / J	0.55	0.56	0.75	0.80	0.59	0.69
$-\Delta U$(carb) / J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	39.69	40.60	40.10	39.83	38.98	38.51
$-\Delta_c u^o$ / J·g^{-1}	29246.46	29233.72	29244.32	29234.11	29232.20	29248.81
$-\langle\Delta_c u^0\rangle$ = (29239.9 ± 3.0) J·g^{-1}						

ε_{cal} = (25165.6 ± 1.5) J·K^{-1}

Table S4 - Standard (p^o = 0.1 MPa) massic energy of combustion of 4-chlorobenzophenone, at T = 298.15 K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.71564	0.73993	0.82622	0.76488	0.73511	0.75543
m'(fuse) / g	0.00276	0.00279	0.00258	0.00250	0.00252	0.00288
ΔT_{ad} / K	0.83494	0.86392	0.96407	0.89282	0.85800	0.88316
ε_i / J·K^{-1}	72.67	72.69	72.78	72.72	72.69	72.71
ε_f / J·K^{-1}	71.77	71.81	71.94	71.83	71.81	71.86
Δm(H_2O) / g	2.3	-0.8	-3.3	-1.9	0.9	0.0
$-\Delta U$(IBP)[a] / J	21080.66	21801.16	24318.46	22526.36	21657.86	22289.65
ΔU(fuse) / J	44.82	45.31	41.90	40.60	40.92	46.77
ΔU(HNO_3) / J	8.12	8.36	7.28	7.16	7.76	17.31
ΔU(As_2O_3) / J	75.17	73.25	64.93	73.25	69.73	88.29
ΔU(ign.) / J	1.28	1.27	1.27	1.29	1.27	1.28
ΔU(H_2PtCl_6) / J	0.45	0.82	0.79	0.69	0.69	0.68
$-\Delta U$(carb) / J	39.28	40.60	45.31	41.96	40.34	41.31
ΔU_Σ / J	29220.75	29234.59	29237.95	29235.19	29243.45	29246.93
$-\Delta_c u^o$ / J·g^{-1} = (29236.5 ± 3.7) J·g^{-1}						

ε_{cal} = (25165.8 ± 1.7) J·K^{-1}

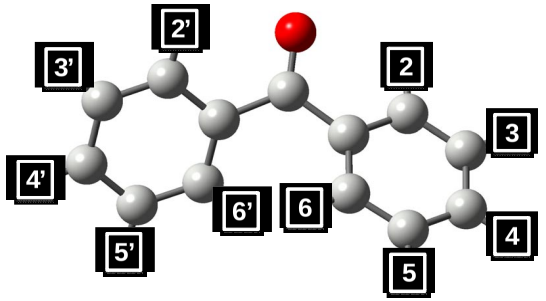
Table S5 - Standard (p^o = 0.1 MPa) massic energy of combustion of 4,4'-dichlorobenzophenone, at T = 298.15 K

Experiment	1	2	3	4	5	6	7	8
m(cpd) / g	0.75289	0.75818	0.75939	0.76382	0.74613	0.75168	0.76029	0.78759
m'(fuse) / g	0.00294	0.00301	0.00321	0.00266	0.00304	0.00257	0.00295	0.00291
ΔT_{ad} / K	0.74360	0.74853	0.75015	0.75494	0.73750	0.74292	0.75171	0.77796
ε_i / J·K^{-1}	114.69	93.73	93.73	93.73	93.72	93.72	93.60	93.62
ε_f / J·K^{-1}	112.19	91.62	91.59	91.56	91.60	91.60	91.62	91.65
$\Delta m(H_2O)$ / g	-3.1	0.6	0.0	-1.6	-0.6	-2.1	-1.0	0.4
$-\Delta U$(IBP)[a] / J	18788.97	18909.28	18948.32	19064.26	18626.93	18759.16	18984.48	19652.00
ΔU(fuse) / J	47.75	48.88	52.13	43.20	49.37	41.74	47.91	47.26
$\Delta U(HNO_3)$ / J	3.22	6.93	3.10	2.51	5.13	5.97	9.19	9.67
$\Delta U(As_2O_3)$ / J	136.54	138.99	143.15	150.83	141.55	142.51	155.37	150.57
ΔU(ign.) / J	1.29	1.28	1.29	1.28	1.29	1.26	1.31	1.31
$\Delta U(H_2PtCl_6)$ / J	1.34	1.54	1.75	1.91	1.78	1.45	2.06	2.14
$-\Delta U$(carb) / J	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta U_{\sum}$ / J	52.07	42.96	43.08	43.28	42.36	42.61	43.16	44.56
$-\Delta_c u^o$ / J·g^{-1}	24634.09	24623.04	24630.06	24640.95	24641.08	24642.96	24629.39	24627.65
$-\langle\Delta_c u^0\rangle$ = (24633.6 ± 2.6) J·g^{-1}								

ε_{cal} = (25165.6 ± 1.5) J·K^{-1}

Table S6.- Full-details of the calculations. Bold & italic is used to enlighten the most stable configurations, please see the Figure.

Chlorine substitution at position:	**Compound name**	**$H_{298.15}$ hartree**	**Working reaction**	**Calculated ΔH_R kJ/mol**	**Estimated ΔH_f kJ/mol**
2	2-Clbf	-1036.22826	(1)	-17.7	37.0
3	3-Clbf	-1036.23400	(1)	-2.6	21.9
4	*4-Clbf*	*-1036.23481*	*(1)*	*-0.5*	*19.8*
5	*3-Clbf*	*-1036.23405*	*(1)*	*-2.5*	*21.8*
6	*2-Clbf*	*-1036.22921*	*(1)*	*-15.2*	*34.5*
2,3	2,3-Cl_2bf	-1495.85523	(2)	-19.7	17.2
2,4	2,4-Cl_2bf	-1495.85965	(3)	-18.3	11.3
2,5	2,5-Cl_2bf	-1495.85956	(4)	-18.5	8.3
2,6	***2,6-Cl_2bf***	***-1495.85802***	***(3)***	***-22.6***	***15.6***
3,4	3,4-Cl_2bf	-1495.86172	(2)	-2.7	0.2
3,5	***3,5-Cl_2bf***	***-1495.86483***	***(3)***	***-4.7***	***-2.3***
3,6	***2,5-Cl_2bf***	***-1495.86065***	***(4)***	***-15.6***	***5.4***
4,5	***3,4-Cl_2bf***	***-1495.86186***	***(2)***	***-2.3***	***-0.2***
4,6	***2,4-Cl_2bf***	***-1495.86036***	***(3)***	***-16.4***	***9.4***
5,6	***2,3-Cl_2bf***	***-1495.85638***	***(2)***	***-16.7***	***14.2***
2,2'	2,2'-Cl_2bf	-1495.85251	(5)	-41.0	29.7
2,3'	2,3'-Cl_2bf	-1495.85989	(5)	-21.6	10.3
2,4'	2,4'-Cl_2bf	-1495.86106	(5)	-18.5	7.2
2,5'	2,3'-Cl_2bf	-1495.86010	(5)	-21.0	9.7
2,6'	2,2'-Cl_2bf	-1495.85363	(5)	-38.0	26.7
3,3'	3,3'-Cl_2bf	-1495.86582	(5)	-6.0	-5.3
3,4'	3,4'-Cl_2bf	-1495.86670	(5)	-3.7	-7.6
3,5'	***3,3'-Cl_2bf***	***-1495.86586***	***(5)***	***-5.9***	***-5.4***
3,6'	2,3'-Cl_2bf	-1495.86111	(5)	-18.4	7.1
4,4'	***4,4'-Cl_2bf***	***-1495.86745***	***(5)***	***-1.7***	***-9.6***
4,5'	***3,4'-Cl_2bf***	***-1495.86673***	***(5)***	***-3.6***	***-7.7***
4,6'	***2,4'-Cl_2bf***	***-1495.86214***	***(5)***	***-15.7***	***4.4***
5,5'	***3,3'-Cl_2bf***	***-1495.86589***	***(5)***	***-5.8***	***-5.5***
5,6'	***2,3'-Cl_2bf***	***-1495.86123***	***(5)***	***-18.1***	***6.8***
6,6'	***2,2'-Cl_2bf***	***-1495.85462***	***(5)***	***-35.4***	***24.1***



Reaction (1): chlorobenzophenone + benzene → benzophenone + chlorobenzene
Reaction (2): dichlorobenzophenone + benzene → benzophenone + 1,2-dichlorobenzene
Reaction (3): dichlorobenzophenone + benzene → benzophenone + 1,3-dichlorobenzene
Reaction (4): dichlorobenzophenone + benzene → benzophenone + 1,4-dichlorobenzene
Reaction (5): dichlorobenzophenone + 2 benzene → benzophenone + 2 chlorobenzene