SUPPLEMENTARY INFORMATION

Experimental and Computational Thermochemical Study of the Three Monofluorophenol Isomers

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This supplementary information includes the details of all the combustion calorimetry experiments performed by rotating bomb for the three fluorophenols studied, as well as, the fully optimized geometries and the calculated energies for the benzene, phenol, fluorobenzene and the 2-, 3- and 4-fluorophenol.

Combustion calorimetry results

Tables S1 to S3 report the details of all experimental determinations of the standard (p° = 0.1 MPa) massic energies of combustion of 2-fluorophenol, 3-fluorophenol and 4-fluorophenol.

The symbols presented in these tables have the following meanings: m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of fuse (cotton) used in each experiment; m''(polyethylene) is the mass of polyethylene 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 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; $\Delta m(H_2O)$ 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); ΔU(polyethylene) is the energy of combustion of polyethylene; ΔU(Melinex) is the energy of combustion of Melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion.

Table S1 - Standard massic energy of combustion of 2-fluorophenol, at $T = 298.15$ K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.53522	0.47252	0.46430	0.41688	0.60298	0.51536
m'(fuse) / g	0.00279	0.00289	0.00304	0.00274	0.00247	0.00271
m''(polyethylene) / g	0.17626	0.18732	0.16670	0.17523	0.17215	0.16362
T_i / K	297.4231	297.3007	297.3502	297.3871	297.1913	297.3166
T_f / K	298.3133	298.1512	298.1547	298.1579	298.1478	298.1670
ΔT_{ad} / K	0.87718	0.83313	0.78705	0.75347	0.93885	0.83337
ε_i / J·K^{-1}	51.62	51.54	51.49	51.43	51.73	51.57
ε_f / J·K^{-1}	53.30	53.17	53.02	52.92	53.47	53.15
ε(calor)$_{corr.}$ / J·K^{-1}	25157.0	25154.1	25158.7	25160.3	25155.7	25157.4
Δm(H_2O) / g	−0.1	−0.8	0.3	0.7	−0.4	0.0
$-\Delta U$(IBP)[a] / J	22111.45	20998.25	19840.39	18994.98	23664.67	21007.11
ΔU(fuse) / J	45.31	46.93	49.37	44.50	40.11	44.01
ΔU(polyethylene) / J	8157.74	8669.62	7715.28	8110.06	7967.52	7572.73
ΔU(HNO_3) / J	4.66	2.15	6.21	2.87	3.70	3.34
ΔU(ign) / J	1.30	1.30	1.27	1.29	1.29	1.29
ΔU_Σ / J	25.21	26.66	26.14	26.91	23.67	25.20
$-\Delta_c u^o$ / J·g^{-1}	25930.51	25930.94	25938.81	25932.26	25920.71	25927.18
$-\left\langle \Delta_c u^o \right\rangle = (25930.1 \pm 2.4)$ J·g^{-1}						

[a] $\Delta U(\text{IBP}) = -\varepsilon(\text{calor})_{corr.} \cdot \Delta T_{ad} + (T_i - 298.15\text{ K}) \cdot \varepsilon_i + (298.15\text{ K} - T_i - \Delta T_{ad}) \cdot \varepsilon_f + \Delta U(\text{ign})$; $\varepsilon(\text{calor})_{corr.} = \varepsilon(\text{calor}) + c_p(H_2O, l) \cdot \Delta m(H_2O, l)$.

Table S2 - Standard massic energy of combustion of 3-fluorophenol, at $T = 298.15$ K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.48034	0.65743	0.57750	0.54623	0.54332	0.50281
m'(fuse) / g	0.00357	0.00278	0.00264	0.00363	0.00290	0.00283
m''(polyethylene) / g	0.19378	0.18241	0.16394	0.18304	0.16692	0.19344
T_i / K	297.2658	297.1193	297.2350	297.2336	297.2697	297.2580
T_f / K	298.1351	298.1484	298.1488	298.1506	298.1538	298.1494
ΔT_{ad} / K	0.85218	1.01216	0.89680	0.90032	0.86753	0.87452
ε_i / J·K^{-1}	51.57	51.51	51.39	51.65	51.62	51.60
ε_f / J·K^{-1}	53.25	53.70	53.33	53.37	53.27	53.30
ε(calor)$_{corr.}$ / J·K^{-1}	25156.6	25159.5	25152.8	25157.0	25157.8	25151.5
$\Delta m(H_2O)$ / g	−0.2	0.5	−1.1	−0.1	0.1	−1.4
$-\Delta U$(IBP)[a] / J	21480.61	25516.39	22601.79	22694.56	21868.80	22039.37
ΔU(fuse) / J	57.98	45.15	42.87	58.95	47.10	45.96
ΔU(polyethylene) / J	8968.60	8442.37	7587.54	8471.53	7725.46	8952.87
$\Delta U(HNO_3)$ / J	2.87	0.24	2.27	2.03	8.96	1.31
ΔU(ign) / J	1.23	1.15	1.29	1.26	1.11	1.22
ΔU_Σ / J	26.76	22.86	23.96	25.23	24.75	26.36
$-\Delta_c u^o$ / J·g^{-1}	25865.85	25867.04	25879.05	25880.71	25882.59	25880.29

$$-\left\langle \Delta_c u^o \right\rangle = (25875.9 \pm 3.0)\ \text{J·g}^{-1}$$

[a] $\Delta U(\text{IBP}) = -\varepsilon(\text{calor})_{corr.} \cdot \Delta T_{ad} + (T_i - 298.15\ \text{K}) \cdot \varepsilon_i + (298.15\ \text{K} - T_i - \Delta T_{ad}) \cdot \varepsilon_f + \Delta U(\text{ign})$; $\varepsilon(\text{calor})_{corr.} = \varepsilon(\text{calor}) + c_p(H_2O, l) \cdot \Delta m(H_2O, l)$.

Table S3 - Standard massic energy of combustion of 4-fluorophenol, at $T = 298.15$ K

Experiment	1	2	3	4	5	6
m(cpd) / g	0.65108	0.71547	0.72460	0.66611	0.66929	0.66029
m'(fuse) / g	0.00259	0.00355	0.00315	0.00251	0.00301	0.00288
m''(Melinex) / g	0.03910	0.04053	0.03932	0.04099	0.04183	0.04093
T_i / K	297.4226	297.4136	297.3462	297.4019	297.4014	297.4151
T_f / K	298.1447	298.2017	298.1439	298.1410	298.1446	298.1483
ΔT_{ad} / K	0.70444	0.77221	0.77979	0.72112	0.72552	0.71641
ε_i / J·K^{-1}	51.22	51.24	51.25	51.18	51.19	51.17
ε_f / J·K^{-1}	52.59	52.73	52.75	52.57	52.60	52.58
ε(calor)$_{corr.}$ / J·K^{-1}	25167.4	25158.7	25161.6	25160.3	25163.3	25147.8
Δm(H_2O) / g	2.4	0.3	1.0	0.7	1.4	−2.3
$-\Delta U$(IBP)[a] / J	17763.68	19466.16	19659.48	18179.18	18292.30	18051.59
ΔU(fuse) / J	42.06	57.65	51.16	40.76	48.88	46.77
ΔU(Melinex) / J	895.47	928.22	900.51	938.75	957.99	937.38
ΔU(HNO_3) / J	2.63	3.94	1.91	2.27	4.66	9.19
ΔU(ign) / J	1.29	1.26	1.21	1.28	1.28	1.18
ΔU_Σ / J	18.60	17.64	17.49	18.39	18.37	18.48
$-\Delta_c u^o$ / J·g^{-1}	25810.84	25799.42	25791.35	25790.05	25792.11	25806.49
$-\left\langle \Delta_c u^o \right\rangle = (25798.4 \pm 3.6)$ J·g^{-1}						

[a] $\Delta U(\text{IBP}) = -\varepsilon(\text{calor})_{corr.} \cdot \Delta T_{ad} + (T_i - 298.15\text{ K}) \cdot \varepsilon_i + (298.15\text{ K} - T_i - \Delta T_{ad}) \cdot \varepsilon_f + \Delta U(\text{ign})$; $\varepsilon(\text{calor})_{corr.} = \varepsilon(\text{calor}) + c_p(H_2O, l) \cdot \Delta m(H_2O, l)$.

Table S4.- B3LYP/6-311++G(d,P) full-optimized geometries of all compounds considered in the present work.

Cartesian coordinates / Å					Compound
C	1	-0.729072	-1.188906	0.000085	Benzene
C	2	0.665093	-1.225841	-0.000053	
C	3	1.394209	-0.036938	-0.000084	
C	4	0.729072	1.188905	0.000163	
C	5	-0.665093	1.225841	-0.000093	
C	6	-1.394208	0.036938	-0.000051	
H	7	-1.295960	-2.113368	0.001377	
H	8	1.182235	-2.179023	-0.000751	
H	9	2.478252	-0.065660	-0.000191	
H	10	1.295960	2.113368	0.000689	
H	11	-1.182233	2.179025	-0.000194	
H	12	-2.478252	0.065662	-0.000723	
C	1	0.938061	-0.023795	0.000108	Phenol
C	2	0.220986	-1.221458	-0.000091	
C	3	-1.169580	-1.188969	0.000025	
C	4	-1.855177	0.027062	0.000093	
C	5	-1.131517	1.217105	-0.000107	
C	6	0.262630	1.197785	-0.000031	
O	7	2.305407	-0.110360	-0.000046	
H	8	0.764264	-2.158657	-0.000066	
H	9	-1.721931	-2.122077	-0.000021	
H	10	-2.938393	0.045261	0.000053	
H	11	-1.649299	2.169753	0.000028	
H	12	0.822487	2.128715	-0.000048	
H	13	2.687205	0.773512	0.000428	
C	1	-0.925121	0.000000	0.000356	Fluorobenzene
C	2	-0.260556	-1.216329	-0.000060	
C	3	1.134349	-1.206965	-0.000197	
C	4	1.832987	0.000000	0.000080	
C	5	1.134349	1.206965	-0.000189	
C	6	-0.260556	1.216329	-0.000067	
F	7	-2.282530	0.000000	-0.000003	
H	8	-0.826489	-2.138994	-0.000310	
H	9	1.673422	-2.147017	0.000130	
H	10	2.916193	0.000000	0.000854	
H	11	1.673422	2.147017	0.000138	
H	12	-0.826489	2.138994	-0.000322	

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Cartesian coordinates / Å					Compound
C	1	0.849622	-0.256780	0.000000	2-Fluorophenol
C	2	0.000000	0.848681	0.000000	
C	3	-1.375887	0.732526	0.000000	
C	4	-1.938210	-0.544673	0.000000	
C	5	-1.109200	-1.665902	0.000000	
C	6	0.277241	-1.527086	0.000000	
F	7	0.591098	2.080567	0.000000	
O	8	2.204783	-0.122891	0.000000	
H	9	-1.984591	1.628344	0.000000	
H	10	-3.015245	-0.657305	0.000000	
H	11	-1.542050	-2.659263	0.000000	
H	12	0.932161	-2.389917	0.000000	
H	13	2.430193	0.815564	0.000000	
C	1	-1.194248	-0.301328	0.000422	3-Fluorophenol
C	2	0.000795	-1.022620	0.000123	
C	3	1.189126	-0.314343	0.000234	
C	4	1.247466	1.072300	0.000152	
C	5	0.041784	1.769071	-0.000179	
C	6	-1.178278	1.095602	0.000046	
F	7	2.350167	-1.013830	-0.000159	
O	8	-2.352714	-1.026378	-0.000394	
H	9	-0.004910	-2.104468	-0.000299	
H	10	2.204910	1.576021	-0.000180	
H	11	0.051303	2.852749	-0.000688	
H	12	-2.110652	1.651061	-0.000036	
H	13	-3.110308	-0.431965	0.000999	
C	1	−1.380036	0.017031	−0.000010	4-Fluorophenol
C	2	−0.672185	1.220397	−0.000003	
C	3	0.718799	1.210000	0.000003	
C	4	1.382855	−0.007521	0.000002	
C	5	0.702406	−1.212306	−0.000006	
C	6	−0.692418	−1.197079	−0.000012	
F	7	2.742454	−0.017206	0.000008	
O	8	−2.748820	0.094416	−0.000016	
H	9	−1.220920	2.153882	−0.000002	
H	10	1.286480	2.132033	0.000009	
H	11	1.253353	−2.144295	−0.000007	
H	12	−1.239484	−2.134728	−0.000018	
H	13	−3.127486	−0.790503	0.000232	

Table S5 – Calculated energies, in Hartree[a]

	E_{el}	$E_{el} + \varepsilon_{ZPE}$	H(298.15 K)
Benzene	–232.311303	–232.212359	–232.207177
Phenol	–307.558730	–307.455961	–307.449610
Phenoxy Radical	–306.909843	–306.819845	–306.813380
Fluorobenzene	–331.580193	–331.489466	–331.483536
2–Fluorophenol	–406.826511	–406.731438	–406.724404
3–Fluorophenol	–406.827507	–406.732823	–406.725710
4–Fluorophenol	–406.825475	–406.730865	–406.723699
2–Fluorophenol Radical	–406.175887	–406.094003	–406.086700
3–Fluorophenol Radical	–406.176475	–406.094676	–406.087460
4–Fluorophenol Radical	–406.179672	–406.097615	–406.090408

[a] Assigned energy corrections to the total energy (in hartrees/particle):
1 hartree = 4.359 75 × 10^{-18} J
ε_{ZPE} = zero point correction; E_{el} = total electronic energy; H(298.15 K) = total electronic energy + zero point energy (scaled to 0.9887) + enthalpy correction (scaled to 0.9688).