

Polymorphism in 4'-Hydroxyacetophenone: Structure and Energetics

Carlos E. S. Bernardes,^a M. Fátima M. Piedade,^{a,b} and Manuel E. Minas da Piedade^{*,a}

^a *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016*

Lisboa, Portugal; E-mail: memp@fc.ul.pt

^b *Centro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico da Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal.*

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

KEYWORDS: 4'-hydroxyacetophenone / polymorphism / X-ray diffraction / crystal structure / energetics / calorimetry / Knudsen effusion / phase diagram

BRIEFS (WORD Style "BH_Briefs"). Polymorphism in 4'-Hydroxyacetophenone: Structure and Energetics

Supporting Information

Table S1: Indexation of the X-ray Powder Diffraction Pattern Recorded at Room Temperature, in the Range $5^\circ \leq 2\theta \leq 35^\circ$, for Monoclinic (Form I) 4'-Hydroxyacetophenone Prepared by Heating the Sublimed HAP Starting Material in an Oven, at 363 K (Space Group $P2_1/c$; $a = 7.707(2)$ Å, $b = 8.335(3)$ Å, $c = 11.282(3)$ Å, $\beta = 95.10(2)^\circ$).

h	k	l	$2\theta(\text{obs})/^\circ$	Rel Int./%	$\Delta 2\theta/^\circ$
1	0	0	11.52	13	0.00
0	1	1	13.15	9	-0.07
0	0	2	15.79	50	0.03
1	1	1	18.04	5	0.02
-1	0	2	18.69	15	-0.02
0	1	2	19.00	16	-0.03
1	0	2	20.40	3	0.01
2	0	0	23.14	30	-0.01
-1	2	0	24.27	3	-0.02
-2	1	0	25.53	21	0.00
-2	1	1	26.11	6	-0.01
-2	0	2	26.92	100	0.00
-1	1	3	27.72	4	0.03
-1	2	2	28.56	4	0.06
2	1	2	31.26	2	0.02
0	1	4	33.61	5	-0.03

Table S2: Indexation of the X-ray Powder Diffraction Pattern Recorded at Room Temperature, in the Range $5^\circ \leq 2\theta \leq 35^\circ$, for the Tubular Crystals of Monoclinic (Form I) 4'-Hydroxyacetophenone (Space Group $P2_1/c$; $a = 7.744(10)$ Å, $b = 8.330(10)$ Å, $c = 11.289(10)$ Å, $\beta = 94.92(11)^\circ$).

h	k	l	$2\theta(\text{obs})/^\circ$	Int. Rel /%	$\Delta 2\theta/^\circ$
1	0	0	11.40	2	-0.06
0	1	1	13.06	40	-0.16
0	0	2	15.69	100	-0.06
0	1	2	19.05	19	0.03
1	0	2	20.29	2	-0.02
0	2	0	21.28	3	-0.04
1	1	2	22.98	12	0.02
-2	1	1	26.01	4	-0.03
-2	0	2	26.82	14	-0.04
-2	2	1	32.22	12	0.13
0	1	4	33.66	4	0.05

Table S3: Indexation of the X-ray Powder Diffraction Pattern Recorded at Room Temperature, in the Range $5^\circ \leq 2\theta \leq 35^\circ$, for Orthorhombic (Form II) 4'-Hydroxyacetophenone (Space Group $P2_12_12_1$; $a = 6.139(2)$ Å, $b = 9.564(3)$ Å, $c = 24.411(7)$ Å).

h	k	l	$2\theta(\text{obs})/^\circ$	Int. Rel /%	$\Delta 2\theta/^\circ$
1	2	0	11.65	14	-0.10
0	1	1	14.84	13	-0.03
0	2	1	16.13	5	-0.02
1	4	0	17.23	100	0.01
1	1	1	17.59	81	0.06
0	3	1	17.96	11	-0.13
2	1	0	18.92	46	0.02
1	3	1	20.36	72	0.01
2	3	0	21.56	20	0.02
1	4	1	22.49	36	-0.04
0	5	1	23.38	27	0.12
1	5	1	25.07	61	-0.01
2	3	1	26.00	47	-0.01
1	7	0	27.22	15	0.02
2	4	1	27.67	28	-0.11
0	0	2	29.08	9	0.01
0	7	1	29.44	7	0.01
2	5	1	29.87	17	-0.04
1	1	2	30.83	13	0.04
3	4	0	31.67	7	0.03
1	3	2	32.54	7	0.01
3	5	0	33.58	4	0.03
1	8	1	34.09	5	-0.01

Combustion calorimetry. The results of the combustion calorimetric experiments are shown in Table S4 where $m(\text{HAP, I})$ is the mass of monoclinic 4'-hydroxyacetophenone (form I); $n(\text{HNO}_3)$ is the amount of substance of nitric acid formed in the bomb process; ε_i and ε_f are the energy equivalents of the bomb contents in the initial and final states of the bomb process, respectively; T_i , and T_f represent the initial and final temperatures of the experiment; ΔT_c is the contribution to the observed temperature rise of the calorimeter proper due to the heat exchanged with the surroundings and the heat dissipated by the temperature sensor; $\Delta_{\text{ign}}U$ is the electrical energy supplied for ignition of the sample; $\Delta_{\text{IBP}}U$ is the internal energy change associated with the bomb process under isothermal conditions, at $T = 298.15$ K; $\Delta_{\Sigma}U$ represents the sum of all corrections necessary to reduce $\Delta_{\text{IBP}}U$ to the standard state (Washburn corrections); $\Delta U(\text{HNO}_3)$ is the energy change associated with the formation of nitric acid; $\Delta U(\text{HAP, cr II})$ is the contribution of monoclinic 4'-hydroxyacetophenone to the energy of the isothermal bomb process; and, finally, $\Delta_c u^\circ (\text{HAP, cr I})$ is the standard massic energy of combustion of monoclinic 4'-hydroxyacetophenone.

The values of T_i , T_f , and ΔT_c were calculated by using a computer program based on the Regnault-Pfaundler method,^{1, 2} and $\Delta_{\text{IBP}}U$ was obtained from:³

$$\Delta_{\text{IBP}}U = \varepsilon_o(T_i - T_f + \Delta T_c) + \varepsilon_i(T_i - 298.15) + \varepsilon_f(298.15 - T_f + \Delta T_c) + \Delta_{\text{ign}}U \quad (\text{S1})$$

The energy equivalent of the calorimeter and its standard deviation, $\varepsilon_o = (1894.66 \pm 0.30) \text{ J} \cdot \text{K}^{-1}$, was determined, in the conventional way, without bomb rotation,⁴⁻⁶ from the combustion of benzoic acid (NIST SRM 39j), whose energy of combustion under certificate conditions was $\Delta_c u_{\text{cert}} = -(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$. The standard state corrections, $\Delta_{\Sigma}U$, were derived as recommended in the literature,³ by using the following data at $T = 298.15$ K: $c_p^\circ = 1.578 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$ (obtained in this work by Calvet-drop microcalorimetry using a

previously described method),⁷ $\rho = 1.247 \text{ g}\cdot\text{cm}^{-3}$ (from the single crystal X-ray diffraction results obtained in this work), and $-(\partial U/\partial p)_T = 0.083 \text{ J}\cdot\text{MPa}^{-1}\cdot\text{g}^{-1}$.⁸ The values of $\Delta U(\text{HNO}_3)$ and $\Delta U(\text{aux})$ were based on $\Delta_f U_m^\circ(\text{HNO}_3, \text{aq}, 0.1 \text{ mol}\cdot\text{dm}^{-3}) = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$.⁹ The standard massic energy of combustion of monoclinic 4'-hydroxyacetophenone was calculated from:

$$\Delta_c u^\circ(\text{HAP, cr I}) = \frac{1}{m(\text{HAP, cr I})} \{ \Delta_{\text{IBP}} U + \Delta_\Sigma U - \Delta U(\text{HNO}_3) \} \quad (\text{S2})$$

The mean value of the standard massic energy of combustion of monoclinic 4'-hydroxyacetophenone indicated in table S4 is $\Delta_c u^\circ(\text{HAP, cr I}) = -28792.62 \pm 1.98 \text{ J}\cdot\text{g}^{-1}$ where the uncertainty quoted represents the standard deviation of the mean. The $\Delta_c u^\circ$ values indicated above refer to the reaction:



and lead to $\Delta_c U_m^\circ(\text{HAP, cr I}) = -(3920.05 \pm 1.62) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_c H_m^\circ(\text{HAP, cr I}) = -(3922.53 \pm 1.62) \text{ kJ}\cdot\text{mol}^{-1}$, at $T = 298.15 \text{ K}$. All uncertainties quoted represent twice the over-all standard deviation of the mean and include the contributions from the energy of combustion of benzoic acid and from the calibration experiments.¹⁰ From the $\Delta_c H_m^\circ$ values indicated above together with $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$ ¹¹ and $\Delta_f H_m^\circ(\text{H}_2\text{O, l}) = -(285.830 \pm 0.040) \text{ kJ}\cdot\text{mol}^{-1}$,¹¹ $\Delta_f H_m^\circ(\text{HAP, cr I}) = -368.9 \pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ was derived.

Table S4. Results of the Combustion Calorimetric Experiments on Monoclinic 4'-**Hydroxyacetophenone (Form I)**

$M(\text{HAP, cr I})/\text{mg}$	32.1416	26.4829	28.4183	18.4921	19.9158
$10^7 \cdot n(\text{HNO}_3)/\text{mol}$	12.9	8.87	9.68	4.84	8.06
$\varepsilon_i/\text{J} \cdot \text{K}^{-1}$	0.90	0.89	0.90	0.88	0.88
$\varepsilon_f/\text{J} \cdot \text{K}^{-1}$	0.94	0.92	0.93	0.90	0.91
T_i/K	298.03575	298.0018	297.98311	297.98412	297.97494
T_f/K	298.58641	298.48174	298.49028	298.36142	298.37136
$\Delta T_c/\text{K}$	0.06116	0.07651	0.07429	0.09531	0.09268
$\Delta_{\text{ign}}U/\text{J}$	1.76	1.76	1.76	1.76	1.76
$-\Delta_{\text{IBP}}U/\text{J}$	926.13	762.97	818.80	532.77	574.00
$\Delta_{\Sigma}U/\text{J}$	0.62	0.50	0.54	0.35	0.37
$-\Delta U(\text{HNO}_3)/\text{J}$	0.08	0.05	0.06	0.03	0.05
$-\Delta U(\text{HAP, cr I})/\text{J}$	925.43	762.42	818.20	532.39	573.58
$-\Delta_c u^\circ(\text{HAP, cr I})/\text{J} \cdot \text{g}^{-1}$	28792.28	28789.14	28791.31	28790.13	28799.25

$$\langle \Delta_c u^\circ(\text{HAP, cr I}) \rangle = -28792.62 \pm 1.98 \text{ J} \cdot \text{g}^{-1}$$

$$\sigma_{\text{over-all}} = 5.95 \text{ J} \cdot \text{g}^{-1}$$

$$\Delta_c U_m^\circ(\text{HAP, cr I}) = -(3920.05 \pm 1.62) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_c H_m^\circ(\text{HAP, cr I}) = -(3922.53 \pm 1.62) \text{ kJ} \cdot \text{mol}^{-1}$$

Solution calorimetry. The results of the solution calorimetric experiments in ethanol are shown in Tables S5 and S6 where m is the mass of sample, ε is the energy equivalent of the calorimeter determined by electrical calibration, ΔT_{ad} is the adiabatic temperature change, Q is the heat associated to the experiment, and $\Delta_{\text{sln}} H_{\text{m}}^{\circ}$ is the standard molar enthalpy of solution. The energy equivalent of the calorimetric system and the adiabatic temperature change were calculated using the SolCal 1.2 program from Thermometric.

Table S5. Results of the Solution Calorimetric Experiments on Monoclinic 4'-Hydroxyacetophenone (Form I)

m/mg	$\varepsilon/\text{J.K}^{-1}$	$-\Delta T_{\text{ad}}/\text{mK}$	Q/J	$\Delta_{\text{sln}} H_{\text{m}}^{\circ}/\text{kJ.mol}^{-1}$
139.14	213.035	65.543	13.963	13.663
138.50	213.753	65.293	13.957	13.720
138.78	214.014	65.756	14.073	13.806
138.99	213.875	65.733	14.059	13.771
139.13	212.177	65.692	13.938	13.640

$$\langle \Delta_{\text{sln}} H_{\text{m}}^{\circ} \rangle = 13.720 \pm 0.063 \text{ kJ.mol}^{-1}$$

Table S6. Results of the Solution Calorimetric Experiments on Orthorhombic 4'-Hydroxyacetophenone (Form II)

m/mg	$\varepsilon/\text{J.K}^{-1}$	$-\Delta T_{\text{ad}}/\text{mK}$	Q/J	$\Delta_{\text{sln}} H_{\text{m}}^{\circ}/\text{kJ.mol}^{-1}$
138.38	212.810	67.367	14.336	14.105
139.28	213.498	68.557	14.637	14.308
139.29	213.687	68.455	14.628	14.298
138.96	213.885	68.271	14.602	14.307
139.43	212.845	67.526	14.373	14.034

$$\langle \Delta_{\text{sln}} H_{\text{m}}^{\circ} \rangle = 14.210 \pm 0.117 \text{ kJ.mol}^{-1}$$

Table S7. Results of Vapor Pressure Measurements on Monoclinic 4'-Hydroxyacetophenone (Form I)^a

<i>T</i> /K	<i>t</i> /s	<i>m</i> /g	<i>p</i> /Pa
318.2	24215	0.53	0.0346
327.2	34326	2.44	0.1139
339.7	35598	9.66	0.4397
344.7	26011	11.33	0.7067
349.8	28057	21.33	1.2285
355.3	27676	35.53	2.0548
362.8	23284	62.29	4.1491
359.5	24446	48.75	3.1404
336.6	31785	6.42	0.3266
332.8	27888	3.23	0.1868
330.2	40113	4.18	0.1675
338.4	32618	7.34	0.3645

^a Dimensions of hole: $A = 2.27 \cdot 10^{-7} \text{ m}^2$, $l = 2.09 \cdot 10^{-5} \text{ m}$ and $r = 2.688 \cdot 10^{-4} \text{ m}$

Table S8. Molecular Energies (E), Thermal Corrections ($E_v+E_r+E_t$), Zero Point Energies (ZPE), Enthalpies, and Gibbs Energies at 298.15 K, from B3LYP/6-31G(d,p) Calculations on HAP. Data in hartree.^{a,b}.

	Conformation of form I	Conformation of form II
E	−460.130340	−460.130617
ZPE	0.142404	0.142406
E_v+E_r+E	0.008946	0.008937
$H^\circ(298.15\text{ K})$	−459.978046	−459.978329
$G^\circ(298.15\text{ K})$	−460.021947	−460.022206

^a $H^\circ(298.15\text{ K}) = E + ZPE + E_v + E_r + E_t + RT$, where E_v , E_r , and E_t represent the vibrational, rotational, and translational contributions. ^b 1 hartree = 2625.49963 kJ·mol^{−1}

Table S9. Rotational Constants (A , B , and C) and Moments of Inertia (I_A , I_B , I_C) Obtained by the B3LYP/6-31G(d,p) Method for the Most Stable Conformation of HAP (Corresponding to Solid Form II).

A/Hz	3.6587×10^9
$I_A/\text{kg} \cdot \text{m}^2$	2.2937×10^{-45}
B/Hz	7.8633×10^8
$I_B/\text{kg} \cdot \text{m}^2$	1.0672×10^{-44}
C/Hz	6.4984×10^8
$I_C/\text{kg} \cdot \text{m}^2$	1.2914×10^{-44}
$I_A I_B I_C/\text{kg}^3 \cdot \text{m}^6$	3.1613×10^{-133}

Table S10. Structural Parameters, Moments of Inertia (I_{int}), and Barrier Heights (V) Used in the Calculation of the Entropic Contributions from the Hindered Internal Rotation of the Methyl Group ($S_{\text{m, irot}}^{\circ}$), for the Most Stable Conformation of HAP (Corresponding to Solid Form II).

$r_{\text{C-H1}}/\text{m}$	1.0955×10^{-10}
$\angle \phi_{\text{C-H1}}$	68.9113
$r_{\text{C-H2}}/\text{m}$	1.0950×10^{-10}
$\angle \phi_{\text{C-H2}}$	68.880
$r_{\text{C-H3}}/\text{m}$	1.0902×10^{-10}
$\angle \phi_{\text{C-H3}}$	71.446
m_{H}/kg	1.67372×10^{-27}
I_{top}	5.2843×10^{-47}
α°	61.131
β°	28.869
γ°	90.000
$\cos \alpha$	0.4828
$\cos \beta$	0.8757
$\cos \gamma$	0
$I_{\text{int}}/\text{kg} \cdot \text{m}^2$	5.2358×10^{-47}
$V/\text{kJ} \cdot \text{mol}^{-1}$	5.5
x	2.02
y	0.26

$$I_{\text{top}} = \sum_i m_{\text{H}} [r_{\text{C-H}i} \sin(\angle \phi_{\text{C-H}i})]^2 \quad (\text{S4})$$

$$I_{\text{int}} = I_{\text{top}} - I_{\text{top}}^2 \left(\frac{\cos \alpha}{I_{\text{A}}} + \frac{\cos \beta}{I_{\text{B}}} + \frac{\cos \gamma}{I_{\text{C}}} \right) \quad (\text{S5})$$

$$x = V / (kT) \quad (\text{S6})$$

$$y = \frac{\sigma_{\text{int}} h}{\sqrt{8\pi kT}} \quad (\text{S7})$$

Table S11. Scaled Vibration Frequencies Calculated by the B3LYP/6-31G(d,p) Method for the Most Stable Conformation of HAP (Corresponding to Solid Form II).^a

ν/cm^{-1}	ν/cm^{-1}
72.48	1 051.89
104.19	1 089.01
188.20	1 146.85
275.49	1 153.52
326.61	1 244.19
377.51	1 264.67
382.98	1 286.92
407.82	1 334.05
455.1	1 343.40
487.49	1 418.74
552.79	1 425.53
576.11	1 435.59
625.15	1 494.45
666.25	1 574.08
702.84	1 598.23
792.72	1 700.78
810.42	2 929.35
816.23	2 990.10
924.82	3 043.02
925.15	3 043.55
943.39	3 075.36
985.97	3 092.16
1 006.17	3 094.12
	3 665.86

^a Scale factor = 0.9608, from reference 12

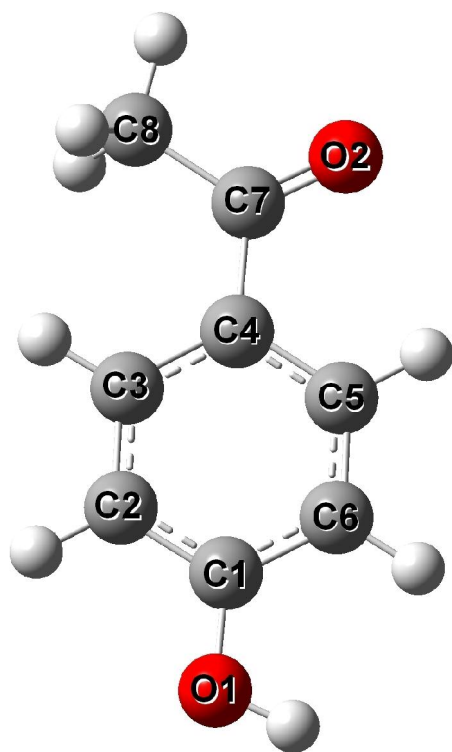


Figure S1. Labeling Scheme Used in the Calculation of the Energy Barriers for Internal Rotation of the CH₃ and OH Groups in HAP

Table S12. Molecular Energies (E) of the Conformations Corresponding to the Methyl group of HAP Internal Rotation and Differences (ΔE) to the Energy of the Most Stable Conformation, as a Function of the θ (C4-C7-C8-H) Dihedral Angle Calculated at the B3LYP/6-31G(d,p) Level of Theory.

θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$	θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$	θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$
60	-460.1306173	0.0	101	-460.1290286	4.2	142	-460.1290914	4.0
61	-460.1306125	0.0	102	-460.1289853	4.3	143	-460.1291412	3.9
62	-460.130605	0.0	103	-460.1289433	4.4	144	-460.1291922	3.7
63	-460.1305949	0.1	104	-460.1289027	4.5	145	-460.1292444	3.6
64	-460.130582	0.1	105	-460.1288637	4.6	146	-460.1292976	3.5
65	-460.1305665	0.1	106	-460.1288265	4.7	147	-460.1293517	3.3
66	-460.1305484	0.2	107	-460.128791	4.8	148	-460.1294066	3.2
67	-460.1305276	0.2	108	-460.1287574	4.9	149	-460.1294622	3.0
68	-460.1305043	0.3	109	-460.1287258	5.0	150	-460.1295183	2.9
69	-460.1304784	0.4	110	-460.1286964	5.0	151	-460.1295747	2.7
70	-460.1304502	0.4	111	-460.128669	5.1	152	-460.1296313	2.6
71	-460.1304196	0.5	112	-460.128644	5.2	153	-460.1296878	2.4
72	-460.1303868	0.6	113	-460.1286213	5.2	154	-460.1297442	2.3
73	-460.1303519	0.7	114	-460.1286012	5.3	155	-460.1298003	2.2
74	-460.1303151	0.8	115	-460.1285835	5.3	156	-460.1298558	2.0
75	-460.1302765	0.9	116	-460.1285685	5.4	157	-460.1299106	1.9
76	-460.1302363	1.0	117	-460.1285561	5.4	158	-460.1299645	1.7
77	-460.1301945	1.1	118	-460.1285463	5.4	159	-460.1300174	1.6
78	-460.1301514	1.2	119	-460.1285391	5.5	160	-460.1300692	1.4
79	-460.1301071	1.3	120	-460.1285346	5.5	161	-460.1301197	1.3
80	-460.1300616	1.5	121	-460.1285327	5.5	162	-460.1301687	1.2
81	-460.130015	1.6	122	-460.1285334	5.5	163	-460.1302162	1.1
82	-460.1299674	1.7	123	-460.1285368	5.5	164	-460.1302618	0.9
83	-460.1299189	1.8	124	-460.1285428	5.5	165	-460.1303055	0.8
84	-460.1298697	2.0	125	-460.1285515	5.4	166	-460.1303469	0.7
85	-460.1298198	2.1	126	-460.128563	5.4	167	-460.1303859	0.6
86	-460.1297693	2.2	127	-460.1285773	5.4	168	-460.1304223	0.5
87	-460.1297184	2.4	128	-460.1285943	5.3	169	-460.1304559	0.4
88	-460.1296673	2.5	129	-460.1286142	5.3	170	-460.1304866	0.3
89	-460.1296159	2.6	130	-460.1286368	5.2	171	-460.1305142	0.3
90	-460.1295645	2.8	131	-460.128662	5.1	172	-460.1305388	0.2
91	-460.1295132	2.9	132	-460.1286899	5.1	173	-460.1305601	0.2
92	-460.129462	3.0	133	-460.1287203	5.0	174	-460.1305782	0.1
93	-460.1294112	3.2	134	-460.1287531	4.9	175	-460.130593	0.1
94	-460.1293607	3.3	135	-460.1287883	4.8	176	-460.1306046	0.0
95	-460.1293109	3.4	136	-460.1288258	4.7	177	-460.1306128	0.0
96	-460.1292617	3.6	137	-460.1288655	4.6	178	-460.1306178	0.0
97	-460.1292132	3.7	138	-460.1289072	4.5	179	-460.1306194	0.0
98	-460.1291655	3.8	139	-460.1289507	4.4			
99	-460.1291188	3.9	140	-460.1289961	4.3			
100	-460.1290732	4.1	141	-460.1290430	4.1			

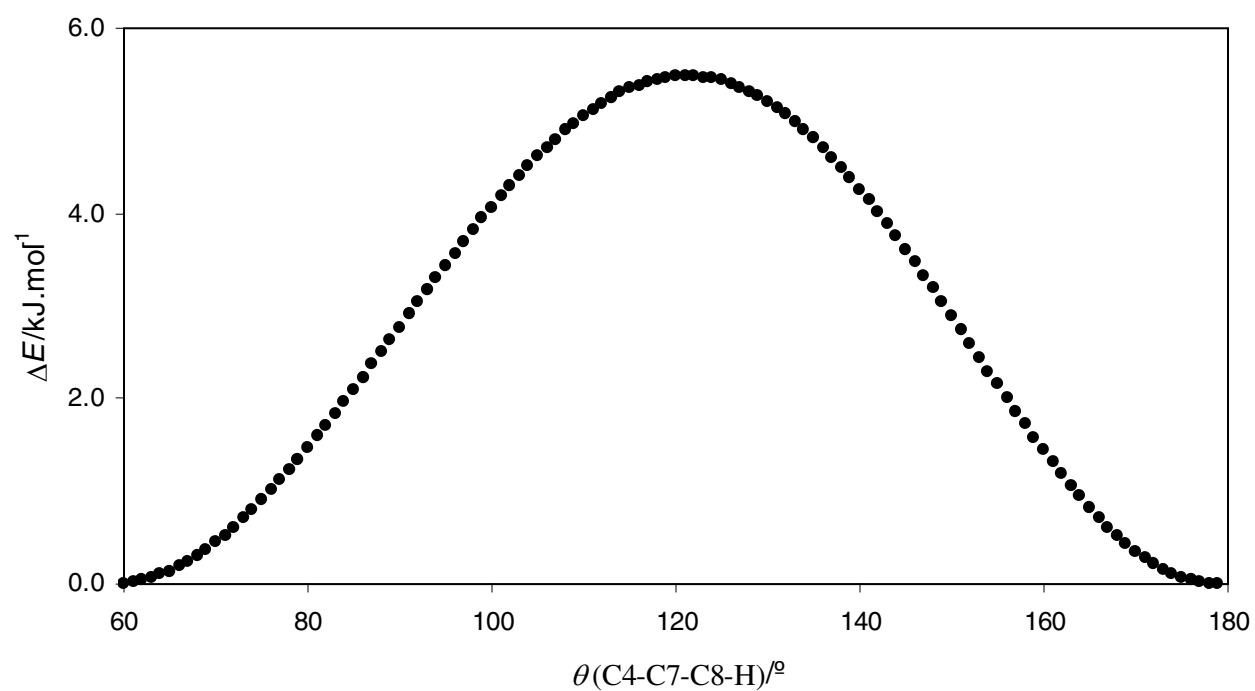


Figure S2. Energy Barrier for Internal Rotation of the Methyl Group of HAP as a Function of the $\theta(\text{C4-C7-C8-H})$ Dihedral Angle (see Table S12, and Figure S1 for Labeling Scheme).

Table S13. Molecular Energies (E) of the Conformations Corresponding to the Hydroxyl group of HAP Internal Rotation and Differences (ΔE) to the Energy of the Most Stable Conformation, as a Function of the θ (C6-C1-O1-H) Dihedral Angle Calculated at the B3LYP/6-31G(d,p) Level of Theory.

θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$	θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}$	θ°	E/Ha	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$
0	-460.1306193	0.0	61	-460.1244586	16.2	122	-460.1249974	14.8
1	-460.1306168	0.0	62	-460.1243402	16.5	123	-460.1251235	14.4
2	-460.1306094	0.0	63	-460.1242241	16.8	124	-460.1252516	14.1
3	-460.1305974	0.1	64	-460.1241114	17.1	125	-460.1253805	13.8
4	-460.1305802	0.1	65	-460.1240013	17.4	126	-460.1255110	13.4
5	-460.1305585	0.2	66	-460.1238950	17.7	127	-460.1256420	13.1
6	-460.1305317	0.2	67	-460.1237916	17.9	128	-460.1257742	12.7
7	-460.1305001	0.3	68	-460.1236923	18.2	129	-460.1259066	12.4
8	-460.1304642	0.4	69	-460.1235962	18.4	130	-460.1260398	12.0
9	-460.1304234	0.5	70	-460.1235044	18.7	131	-460.1261729	11.7
10	-460.1303779	0.6	71	-460.1234160	18.9	132	-460.1263067	11.3
11	-460.1303282	0.8	72	-460.1233322	19.1	133	-460.1264400	11.0
12	-460.1302738	0.9	73	-460.1232518	19.3	134	-460.1265738	10.6
13	-460.1302148	1.1	74	-460.1231762	19.5	135	-460.1267067	10.3
14	-460.1301519	1.2	75	-460.1231044	19.7	136	-460.1268397	9.9
15	-460.1300843	1.4	76	-460.1230375	19.9	137	-460.1269717	9.6
16	-460.1300122	1.6	77	-460.1229746	20.1	138	-460.1271032	9.2
17	-460.1299366	1.8	78	-460.1229170	20.2	139	-460.1272334	8.9
18	-460.1298564	2.0	79	-460.1228634	20.4	140	-460.1273628	8.5
19	-460.1297719	2.2	80	-460.1228153	20.5	141	-460.1274906	8.2
20	-460.1296844	2.5	81	-460.1227714	20.6	142	-460.1276174	7.9
21	-460.1295925	2.7	82	-460.1227330	20.7	143	-460.1277422	7.6
22	-460.1294972	2.9	83	-460.1226990	20.8	144	-460.1278659	7.2
23	-460.1293982	3.2	84	-460.1226707	20.9	145	-460.1279874	6.9
24	-460.1292961	3.5	85	-460.1226467	20.9	146	-460.1281076	6.6
25	-460.1291904	3.8	86	-460.1226285	21.0	147	-460.1282252	6.3
26	-460.1290817	4.0	87	-460.1226147	21.0	148	-460.1283412	6.0
27	-460.1289697	4.3	88	-460.1226067	21.0	149	-460.1284544	5.7
28	-460.1288551	4.6	89	-460.1226031	21.0	150	-460.1285657	5.4
29	-460.1287373	4.9	90	-460.1226054	21.0	151	-460.1286739	5.1
30	-460.1286172	5.3	91	-460.1226122	21.0	152	-460.1287800	4.8
31	-460.1284943	5.6	92	-460.1226247	21.0	153	-460.1288828	4.6
32	-460.1283694	5.9	93	-460.1226416	20.9	154	-460.1289832	4.3
33	-460.1282420	6.2	94	-460.1226643	20.9	155	-460.1290801	4.0
34	-460.1281130	6.6	95	-460.1226913	20.8	156	-460.1291745	3.8
35	-460.1279818	6.9	96	-460.1227240	20.7	157	-460.1292652	3.6
36	-460.1278492	7.3	97	-460.1227609	20.6	158	-460.1293533	3.3
37	-460.1277147	7.6	98	-460.1228034	20.5	159	-460.1294376	3.1
38	-460.1275791	8.0	99	-460.1228501	20.4	160	-460.1295190	2.9
39	-460.1274418	8.3	100	-460.1229021	20.3	161	-460.1295964	2.7
40	-460.1273038	8.7	101	-460.1229581	20.1	162	-460.1296708	2.5

41	-460.1271645	9.1	102	-460.1230193	20.0	163	-460.1297409	2.3
42	-460.1270248	9.4	103	-460.1230842	19.8	164	-460.1298079	2.1
43	-460.1268841	9.8	104	-460.1231540	19.6	165	-460.1298706	2.0
44	-460.1267436	10.2	105	-460.1232273	19.4	166	-460.1299300	1.8
45	-460.1266025	10.5	106	-460.1233053	19.2	167	-460.1299849	1.7
46	-460.1264618	10.9	107	-460.1233867	19.0	168	-460.1300365	1.5
47	-460.1263209	11.3	108	-460.1234724	18.8	169	-460.1300836	1.4
48	-460.1261808	11.7	109	-460.1235613	18.5	170	-460.1301273	1.3
49	-460.1260406	12.0	110	-460.1236545	18.3	171	-460.1301664	1.2
50	-460.1259015	12.4	111	-460.1237505	18.0	172	-460.1302021	1.1
51	-460.1257627	12.8	112	-460.1238505	17.8	173	-460.1302331	1.0
52	-460.1256253	13.1	113	-460.1239532	17.5	174	-460.1302607	0.9
53	-460.1254886	13.5	114	-460.1240594	17.2	175	-460.1302835	0.9
54	-460.1253536	13.8	115	-460.1241680	16.9	176	-460.1303028	0.8
55	-460.1252197	14.2	116	-460.1242798	16.6	177	-460.1303172	0.8
56	-460.1250880	14.5	117	-460.1243936	16.3	178	-460.1303281	0.8
57	-460.1249576	14.9	118	-460.1245103	16.0	179	-460.1303341	0.7
58	-460.1248297	15.2	119	-460.1246288	15.7	180	-460.1303366	0.7
59	-460.1247035	15.5	120	-460.1247499	15.4			
60	-460.1245801	15.9	121	-460.1248725	15.1			

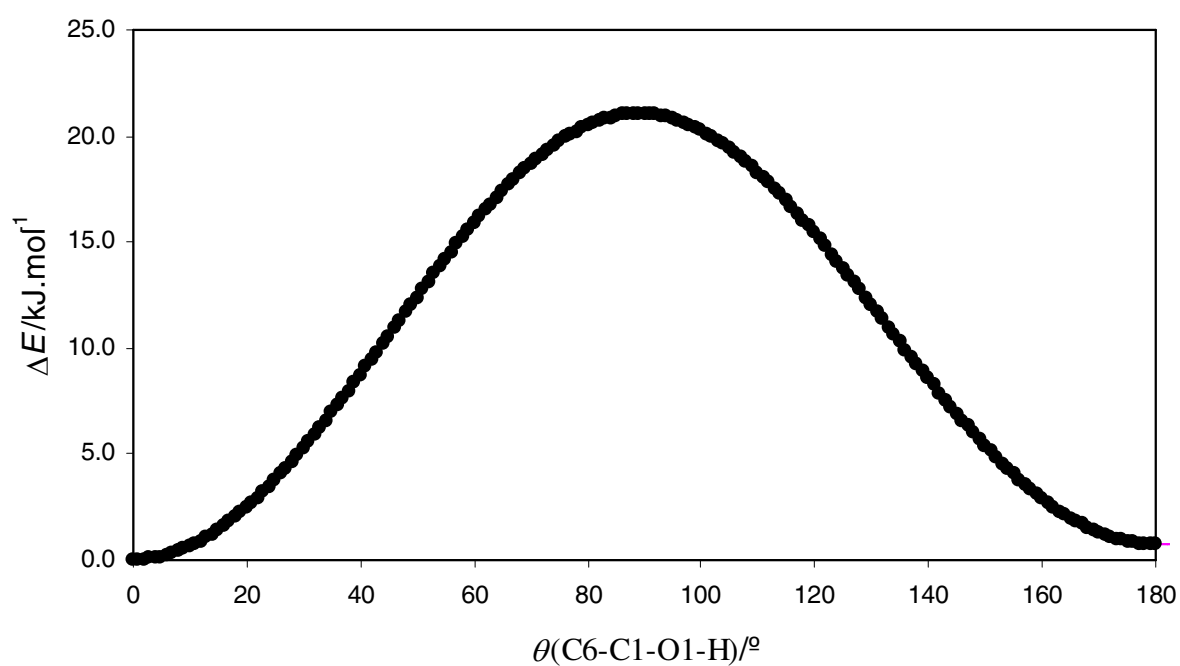


Figure S3. Energy Barrier for Internal Rotation of the Hydroxyl Group of HAP as a Function of the $\theta(\text{C6-C1-O1-H})$ Dihedral Angle (see Table S13, and Figure S1 for Labeling Scheme).

Table S14. Auxiliary Data for the Calculation of the $\Delta_f G_m^0$ - T Diagram ($p^0 = 1$ bar), for the Solid and Liquid Phases of 4'-Hydroxyacetophenone.

M	136.1479 g·mol ⁻¹
R	8.314472 J·K ⁻¹ ·mol ⁻¹
p^0	100000 Pa
$C_{p,m}^0$ (cr I)	214.8 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (cr II)	214.1 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (l)	267.7 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (g)	$= -1.9376 \times 10^{-4} T^2 + 0.5596T + 6.8932$ (J·K ⁻¹ ·mol ⁻¹)
$C_{p,m}^0$ (O ₂ , g) ^a	29.40 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (H ₂ , g) ^a	28.97 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (graphite, s) ^b	9.36 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (O ₂ , g) ^c	30.33 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (H ₂ , g) ^c	29.15 J·K ⁻¹ ·mol ⁻¹
$C_{p,m}^0$ (graphite, s) ^c	11.37 J·K ⁻¹ ·mol ⁻¹
$\Delta_f C_p$ (cr I)	-5.36 J·K ⁻¹ ·mol ⁻¹
$\Delta_f C_p$ (cr II)	-6.11 J·K ⁻¹ ·mol ⁻¹
$\Delta_f C_p$ (l)	29.81 J·K ⁻¹ ·mol ⁻¹
$T_{\text{trs}}(\text{II} \rightarrow \text{I})$	351.2 K
$\Delta_{\text{trs}} H_m(\text{II} \rightarrow \text{I}, 351.2 \text{ K})$	0.53 kJ·mol ⁻¹
$\Delta_{\text{trs}} H_m(\text{II} \rightarrow \text{I}, 298.15 \text{ K})$	0.49 kJ·mol ⁻¹
$\Delta_{\text{fus}} H_m(\text{cr I}, 381.9 \text{ K})$	18.08 kJ·mol ⁻¹
$\Delta_{\text{sub}} H_m(\text{cr I}, 327.4 \text{ K})$	101.82 kJ·mol ⁻¹
S_m^0 (g, 327.4 K)	408.758 J·K ⁻¹ ·mol ⁻¹
$p_{\text{sat}}(\text{cr I}, 327.4 \text{ K})$	0.1104 Pa
S_m^0 (cr I, 327.4 K)	211.850 J·K ⁻¹ ·mol ⁻¹
$\Delta_f H^0(\text{cr I}, 298.15 \text{ K})$	-368.9 kJ·mol ⁻¹

^a Mean value in the range 298 - 347 K obtained from reference 13; ^b Mean value in the range 298 - 347 K obtained from reference 14. ^c Value at the reference temperature 381.9 K obtained from references 13 and 14

Table S15. Details of the Calculation of the $\Delta_f G_m^\circ - T$ (Figure 11a), $\Delta_{\text{trs}} H_m^\circ - T$, $T \Delta_{\text{trs}} S_m^\circ - T$, and $\Delta_{\text{trs}} G_m^\circ - T$ (Figure 11b) Diagrams for the Solid and Liquid Phases of 4'-Hydroxyacetophenone.

T/K	$p_{\text{sat}}(\text{cr I})/\text{Pa}$	$\Delta_f H_m^\circ(\text{cr I})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{cr II})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{l})/\text{kJ}\cdot\text{mol}^{-1}$	$S_m^\circ(\text{g})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_m^\circ(\text{cr I})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_m^\circ(\text{cr II})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_m^\circ(\text{l})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f G_m^\circ(\text{cr I})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G_m^\circ(\text{cr II})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G_m^\circ(\text{l})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{trs}} G_m^\circ/\text{J}\cdot\text{mol}^{-1}$	$\Delta_{\text{trs}} H_m^\circ/\text{J}\cdot\text{mol}^{-1}$	$T \Delta_{\text{trs}} S_m^\circ/\text{J}\cdot\text{mol}^{-1}$
280	0.0002	-368.803	-369.279	-354.307	384.040	178.215	176.864	209.138	-418.703	-418.801	-412.866	98	476	378
285	0.0004	-368.830	-369.310	-354.157	386.682	182.017	180.654	213.877	-420.705	-420.796	-415.112	91	480	388
290	0.0009	-368.856	-369.340	-354.008	389.316	185.752	184.377	218.532	-422.724	-422.809	-417.382	85	484	399
295	0.0018	-368.883	-369.371	-353.859	391.942	189.424	188.037	223.109	-424.763	-424.842	-419.676	79	488	409
298.15	0.0028	-368.900	-369.390	-353.765	393.592	191.706	190.311	225.952	-426.057	-426.131	-421.133	74	490	416
300	0.0036	-368.910	-369.401	-353.710	394.560	193.034	191.636	227.608	-426.82	-426.892	-421.992	72	491	419
305	0.0071	-368.937	-369.432	-353.561	397.169	196.585	195.175	232.033	-428.895	-428.96	-424.331	65	495	430
310	0.0135	-368.964	-369.462	-353.412	399.770	200.078	198.656	236.386	-430.988	-431.045	-426.692	57	498	441
315	0.0253	-368.990	-369.493	-353.263	402.363	203.515	202.082	240.669	-433.097	-433.149	-429.074	52	503	451
320	0.0465	-369.017	-369.524	-353.114	404.948	206.897	205.453	244.885	-435.224	-435.269	-431.477	45	507	462
325	0.0838	-369.044	-369.554	-352.965	407.524	210.228	208.773	249.035	-437.368	-437.405	-433.901	37	510	473
327.4	0.1104	-369.057	-369.569	-352.894	408.758	211.808	210.348	251.005	-438.403	-438.437	-435.073	34	512	478
330	0.1483	-369.071	-369.585	-352.816	410.092	213.507	212.042	253.122	-439.528	-439.559	-436.346	31	514	483
335	0.2580	-369.098	-369.615	-352.667	412.652	216.737	215.261	257.148	-441.705	-441.727	-438.812	22	517	494
340	0.4416	-369.124	-369.646	-352.518	415.203	219.919	218.433	261.114	-443.896	-443.913	-441.297	17	522	505
345	0.7443	-369.151	-369.676	-352.369	417.746	223.055	221.559	265.022	-446.105	-446.114	-443.802	9	525	516
347	0.9132	-369.162	-369.688	-352.309	418.761	224.297	222.796	266.569	-446.993	-446.998	-444.808	5	526	521
350	1.2358	-369.178	-369.707	-352.220	420.281	226.146	224.639	268.874	-448.329	-448.331	-446.326	2	529	527
351.2	1.3927	-369.184	-369.714	-352.184	420.888	226.881	225.372	269.790	-448.865	-448.865	-446.934	0	530	530
352	1.5076	-369.189	-369.719	-352.160	421.293	227.370	225.859	270.399	-449.223	-449.221	-447.34	-2	530	532
355	2.0228	-369.205	-369.737	-352.071	422.808	229.193	227.676	272.671	-450.569	-450.562	-448.869	-7	532	539
360	3.2661	-369.232	-369.768	-351.922	425.326	232.197	230.671	276.415	-452.823	-452.81	-451.431	-13	536	549
365	5.2048	-369.258	-369.798	-351.773	427.836	235.160	233.624	280.108	-455.091	-455.071	-454.012	-20	540	561
370	8.1905	-369.285	-369.829	-351.624	430.338	238.082	236.537	283.750	-457.375	-457.348	-456.612	-27	544	572
375	12.7339	-369.312	-369.860	-351.475	432.831	240.966	239.411	287.343	-459.674	-459.639	-459.229	-35	548	583
380	19.5690	-369.339	-369.890	-351.326	435.317	243.811	242.246	290.889	-461.987	-461.943	-461.864	-44	551	595
381.9	22.9720	-369.349	-369.902	-351.269	436.259	244.882	243.314	292.224	-462.869	-462.824	-462.869	-45	553	599
385	29.7392	-369.366	-369.921	-351.176	437.794	246.619	245.045	294.388	-464.314	-464.263	-464.515	-51	555	606
390	44.7126	-369.392	-369.951	-351.027	440.262	249.390	247.808	297.843	-466.654	-466.596	-467.186	-58	559	617
395	66.5346	-369.419	-369.982	-350.878	442.723	252.127	250.535	301.253	-418.703	-418.801	-412.866	-66	563	629

References

1. Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodynamics* **1995**, 27, 197-206.
2. Santos, R. C.; Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodynamics* **1999**, 31, 1417-1427.
3. Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*, Rossini, F. D., Ed. Interscience: New York, 1956; Vol. 1, Chapter 5.
4. Coops, J.; Jessup, R. S.; van Nes, K. In *Experimental Thermochemistry*, Rossini, F. D., Ed. Interscience: New York, 1956; Vol. 1, Chapter 3.
5. Mosselman, C.; Churney, K. L. In *Experimental Chemical Thermodynamics*, Sunner, S.; Månsson, M., Eds. Pergamon Press: London, 1979; Vol. 1, pp 35-55.
6. Cordfunke, E. H. P.; Ouweltjes, H. In *Experimental Thermodynamics*, Marsh, K. N.; O'Hare, P. A. G., Eds. Pergamon Press: London, 1994; Vol. IV; Chapter 14.
7. Bernardes, C. E. S.; Santos, L. M. N. B. F.; Minas da Piedade, M. E. *Meas. Sci. Technol.* **2006**, 17, 1405-1408.
8. Calculated as $(du/dp)_T = -(dV/dT)_p$, by using the density against temperature data for form I of HAP obtained in this work from single crystal X-ray diffraction experiments.
9. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamics Properties, J. Phys Chem. Ref. Data* **1982**, 11, Supplement no. 2.
10. Olofsson, G. *Assignment of Uncertainties*; In *Experimental Chemical Thermodynamics*, Sunner, S.; Månsson, M., Eds. Pergamon Press: Oxford, 1979; Vol. 1, pp 137-159.
11. Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *Codata Key Values for Thermodynamics*; Hemisphere: New York, 1989.
12. Computational Chemistry Comparison and Benchmark DataBase. In *NIST Standard Reference Database 101 (Release 12)*, National Institute of Standards and Technology: Gaithersburg, 2005.
13. Chase Jr., M. W. *NIST-JANAF Thermochemical Tables*; 4th ed.; *J. Phys. Chem. Ref. Data* **1998**, Monograph 9.
14. Butland, A. T. D.; Maddison, R. J. *J. Nucl. Mater.* **1973**, 49, 45-56.