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Thermochemistry of chromone- and coumarin-3-carboxylic acid

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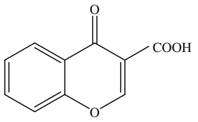
Abstract The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed state of chromone-3-carboxylic acid and coumarin-3-carboxylic acid were derived from the standard molar energies of combustion in oxygen at $T = 298.15$ K, measured by combustion calorimetry. The standard molar enthalpies of sublimation were obtained by Calvet microcalorimetry. From these values the standard molar enthalpies in the gaseous phase, at $T = 298.15$ K, were derived. Additionally estimates of the enthalpies of formation, of all the studied compounds in gas-phase, were performed using DFT and other more accurate correlated calculations (MCCM and G3MP2), together with appropriate isodesmic, homodesmic or atomization reactions. There is a reasonable agreement between computational and experimental results.

Keywords Thermochemistry · Enthalpy of formation · Combustion calorimetry · Calvet microcalorimetry · DFT and MCCM calculations

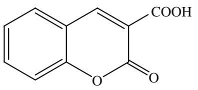
Introduction

Chromones are a class of compounds with a large distribution on nature and a huge number of applications and properties. They have potent effects in preventing both earlier and late asthmatic responses to inhaled allergens, such as pollen, and reducing airway reactivity to a range of inhaled irritants [1–3].

In the present study, we report the standard molar enthalpies of formation of chromone-3-carboxylic acid and coumarin-3-carboxylic acid in the gas-phase, at $T = 298.15$ K. This results were obtained from measurements of combustion energies, at $T = 298.15$ K, using a static bomb calorimeter. The standard molar enthalpies of sublimation were measured by Calvet microcalorimetry.



Chromone-3-carboxylic acid



Coumarin-3-carboxylic acid

We also present estimates of the enthalpies of formation of the two isomers in gas-phase, using DFT and also other more accurate composite correlated calculations, MCCM and G3MP2, together with appropriate isodesmic, homodesmic or atomization reactions.

Additionally the NICS values are discussed comparatively to the non substituted chromone and coumarin.

Experimental section

Materials and DSC

Chromone-3-carboxylic acid [CAS 39079-62-4] and coumarin-3-carboxylic acid [CAS 531-81-7] are commercial products from Aldrich Chemical Co. [4]. The samples were purified by repeated sublimation under reduced pressure before the

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Table 1 Temperatures of fusion, T_{fus}, enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{0}(T_{\text{fus}})$, and purity of chromone-3-carboxylic acid and coumarin-3-carboxylic acid

Compound	T_{fus}/K	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{0}(T_{\text{fus}})$/kJ mol^{-1}	Purity/%
Chromone-3-carboxylic acid	473.21 ± 0.48	31.42 ± 0.38	99.80 ± 0.08
Coumarin-3-carboxylic acid	463.11 ± 0.11	30.95 ± 0.13	99.57 ± 0.03

experimental studies. The purity of the two isomers (Table 1) was derived from DSC (Setaram DSC 141) analysis by a fractional fusion technique [5]. The samples, hermetically sealed in stainless steel crucibles, were heated at 1.67×10^{-2} K s^{-1}. The temperature scale of the calorimeter was calibrated by measuring the melting temperature of three high purity reference materials (naphthalene, benzoic acid and indium) [6] and its power scale was calibrated with high-purity indium (mass fraction > 0.99999). The recorded thermograms for both compounds did not show any phase transitions between 298 K and the melting temperature of the compounds.

The purity of the samples was also confirmed through the carbon dioxide gravimetry results. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered after each combustion experiment to that calculated from the mass of sample were: chromone-3-carboxylic acid (0.9998 ± 0.01) and chromone-3-carboxylic acid (1.0000 ± 0.01). The densities of the samples were estimated, from the mass and the dimensions of pellets of the crystalline compounds, as chromone-3-carboxylic acid (1.13 g cm^{-3}) and coumarin-3-carboxylic acid (1.17 g cm^{-3}).

Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter, using a twin valve bomb, type 1108 of Parr Instrument Company. The apparatus and technique have been described previously [7, 8] so only a brief description is made here. Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190 p) was used for calibration of the bomb. Its massic energy of combustion under certificate conditions is $\Delta_c u = -(26435.1 \pm 3.5)$ J g^{-1}. The calibration results were corrected to give the energy equivalent ε_{cal} corresponding to the average mass of water added to the calorimeter, 3119.6 g. From six independent calibration experiments performed $\varepsilon_{\text{cal}} = (16004.8 \pm 1.6)$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

The compounds were burnt in pellet form. Combustion experiments were made in oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of water added to the bomb. The electrical energy for ignition, ΔU(ign.), was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. As samples were ignited at $T = 298.15$ K,

$$\Delta U(\text{IBP}) = -\{\varepsilon_{\text{cal}} + \Delta m(\text{H}_2\text{O}) \cdot c_p(\text{H}_2\text{O, l}) + \varepsilon_f\}\,\Delta T_{\text{ad}} + \Delta U_{\text{ign}} \quad (1)$$

where ΔU(IBP) is the energy associated to the isothermal bomb process, ε_{f}, is the energy of the bomb contents after ignition and ΔT_{ad} is the adiabatic temperature raise calculated using the program LABTERMO [9]. For the cotton-thread fuse, empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, the value of -16250 J g^{-1} [10] was taken for the massic energy of combustion, $\Delta_c u^0$ (the value has been confirmed in our laboratory). The corrections for nitric acid formation $\Delta U(\text{HNO}_3)$ were based on -59.7 kJ mol^{-1} [11] for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). The mass of compound, m(compound), used in each experiment was determined from the total mass of carbon dioxide, $m(\text{CO}_2$, total), produced after allowance for that formed from the cotton thread fuse.

An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2$ J g^{-1} MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds, was assumed [12]. For each compound, the corrections to the standard state, ΔU_Σ, to derive the standard massic energy of combustion, $\Delta_c u^0$, were made by the procedure given by Hubbard et al. [13]. The atomic weights of the elements were those recommended by the IUPAC commission in 2005 [14].

Microcalorimetry calvet

The standard molar enthalpies of sublimation were measured using the "vacuum sublimation" drop microcalorimetric method [15]. The microcalorimeter was calibrated in situ for these measurements using the reported enthalpy of sublimation of naphthalene [16] Samples, of about 3–5 mg of the compounds contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter (SETARAM HT 1000D) held at $T = 444$ K for chromone-3-carboxylic acid and at $T = 453$ K for coumarin-3-carboxylic acid and then removed from the hot zone by vacuum evaporation. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized, as far as possible, by dropping tubes of nearly equal mass into each of the twin calorimeter cells. From six independent experiments for each compound a mean value was obtained for the observed standard molar enthalpy of sublimation, $\Delta_{\mathrm{cr},298.15\mathrm{K}}^{\mathrm{g},T}H_{\mathrm{m}}^{0}$, which was then corrected to $T = 298.15$ K, $\Delta_{298.15K}^{T}H_{\mathrm{m}}^{0}(\mathrm{g})$, using the equation:

$$\Delta_{298.15K}^{T}H_{\mathrm{m}}^{0}(\mathrm{g}) = \int_{298.15K}^{T} C_{p,m}^{0}(\mathrm{g})\mathrm{d}T \tag{2}$$

where T is the temperature of the hot reaction vessel, $C_{p,m}^{0}(g)$ is the molar heat capacity of the compound in the gas phase and was obtained from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP functional and the 6-31G* basis set:

Chromone-3-carboxylic acid

$$C_{p,m}^{0}(\mathrm{g})/(\mathrm{J\,mol^{-1}K^{-1}}) = -0.000474(T/K)^{2} + 0.837(T/K) - 28.573 \tag{3}$$

Coumarin-3-carboxylic acid

$$C_{p,m}^{0}(\mathrm{g})/(\mathrm{J\,mol^{-1}K^{-1}}) = -0.000485(T/K)^{2} + 0.847(T/K) - 30.648 \tag{4}$$

Computational details

The geometries of all molecules have been fully optimized using density functional theory (DFT) with the Becke 3-parameter hybrid exchange [17] and the Lee–Yang–Parr [18] correlation density functionals (B3LYP) and the Pople's split-valence 6-31G* extended basis set [19, 20]. The optimum structures so obtained where further certified as true minima by constructing and diagonalizing the corresponding Cartesian hessian matrix, this procedure providing also the harmonic vibrational frequencies which, after properly scaled by the recommended scaling factor 0.9614, [21] allow reliable calculations of the thermal corrections to the molecular energy. We have further refined the optimum structures by reoptimizing them using the same methodology with the Pople's split-valence 6-311G** extended basis set [22, 23]. These final optimized structures where then used to perform single point DFT calculations with the cc-pVTZ basis set [24–27] and also energy calculations based on more accurate correlated computational techniques of the MCCM/3 suite [28, 29] and of the Gaussian series, namely G3MP2 calculations[30]. In addition we have studied the main electronic interactions contributing to the stabilization of the molecules by analysing the corresponding restricted Hartree–Fock wave functions, HF/6-311G**, by using Natural Bonding Orbitals (NBO) procedures [31–33].

All the geometry optimizations, vibrational analysis and single point calculations have been performed using the UK version of program GAMESS [34, 35]. The MCCM series of calculations have been performed using the MLGAUSS program version 2.0 [36], which rely on the Gaussian 03 series of programs [37].

The Nucleus Independent Chemical Shifts (NICS) values were calculated using B3LYP/6-311G** wave functions at the B3LYP/6-311G** geometries. The methodology used was developed by Schleyer and his coworkers as a mean of providing useful aromaticity indices [38]. Two different values were calculated for each ring and each molecule: one at the geometrical centre of the ring (i.e. the point whose coordinates are the nonweighted mean of the homologous coordinates of the heavy atoms of the rings), denoted NICS(0) and 1.0 Å above the center of the ring, denoted NICS(1.0). The calculation of NICS values has been performed with the Gaussian 03 series of programs [37] and all NBO analyses were made with the program NBO 5.0 [39].

Experimental results

The temperature of fusion of chromone-and coumarin-3-carboxylic acid was measured using a differential scanning calorimeter. The results (observed at the onset temperature of the calorimetric peak), T_{fus}, are presented in Table 1 together with the enthalpies of fusion, at the temperatures of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{0}(T_{\mathrm{fus}})$, and the purity of the purified sample. Those values represent the mean values of six independent experiments on fresh samples and the uncertainties are twice the standard deviation of the mean.

Results for a typical combustion experiment of the two isomers are given in Table 2. The values of the massic energy of combustion, $\Delta_{\mathrm{c}}u^{0}$, refer to the combustion reaction:

Table 2 Typical combustion experiments, at $T = 298.15$ K

	Chromone-3-carboxylic	Coumarin-3-carboxylic
$m(\mathrm{CO_2}, \mathrm{total})/\mathrm{g}$	1.59701	1.45361
$m(\mathrm{cpd})/\mathrm{g}$	0.68818	0.62624
$m(\mathrm{fuse})/\mathrm{g}$	0.00264	0.00262
$\Delta T_{\mathrm{ad}}/\mathrm{K}$	0.9457	0.8550
$\varepsilon_{\mathrm{f}}/(\mathrm{J\ K^{-1}})$	15.65	15.28
$\Delta m(\mathrm{H_2O})/\mathrm{g}$	0.0	0.0
$-\Delta U(\mathrm{IBP})/\mathrm{J}$	15149.43	13696.09
$\Delta U(\mathrm{fuse})/\mathrm{J}$	42.87	42.55
$\Delta U(\mathrm{HNO_3})/\mathrm{J}$	7.57	5.47
$\Delta U(\mathrm{ign.})/\mathrm{J}$	1.11	1.08
$\Delta U_{\Sigma}/\mathrm{J}$	13.56	12.24
$-\Delta_{\mathrm{c}}u^{0}/(\mathrm{J\ g^{-1}})$	21920.76	21774.13

Table 3 Individual values of the massic energy of combustion, at $T = 298.15$ K

Chromone-3-carboxylic acid	Coumarin-3-carboxylic acid
$-\Delta_c u^0/(\text{J g}^{-1})$	
21920.76	21774.13
21905.03	21767.13
21934.40	21785.91
21902.04	21763.65
21921.51	21772.97
21918.21	21774.98
21912.25	21769.79
–	21779.36
$-\langle\Delta_c u^0\rangle/(\text{J g}^{-1})$	
21916.3 ± 4.2	21773.4 ± 2.5

Table 4 Derived standard ($p^\circ = 0.1$ MPa) molar values, at $T = 298.15$ K

Compound	$-\Delta_c U_m^0$/kJ mol^{-1}	$-\Delta_c H_m^0$/kJ mol^{-1}	$-\Delta_f H_m^0$(cr)/kJ mol^{-1}
Chromone-3-carboxylic acid	4167.5 ± 1.9	4166.3 ± 1.9	626.3 ± 2.3
Coumarin-3-carboxylic acid	4140.3 ± 1.4	4139.1 ± 1.4	653.5 ± 1.9

$$C_{10}H_6O_4(\text{cr}) + 19/2O_2(\text{g}) \rightarrow 10CO_2(\text{g}) + 3H_2O(\text{l}) \qquad (5)$$

The individual results of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in Table 3. Table 4 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for the compounds in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical practice, [40] the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities. To derive $\Delta_f H_m^0(\text{cr})$ from $\Delta_c H_m^0(\text{cr})$ the following standard molar enthalpies of formation, at $T = 298.15$ K, were used for H_2O(l), −(285.830 ± 0.042) kJ mol^{-1} [41]; CO_2(g) and −(393.51 ± 0.13) kJ mol^{-1} [42].

Measurements of the standard molar enthalpies of sublimation for the isomers are given in Table 5 with uncertainties of twice the standard deviation of the mean.

The derived standard molar enthalpies of formation, in both condensed and gaseous phases, at $T = 298.15$ K, are summarized in Table 6.

Computational results and discussion

Structurally both chromone-3-carboxylic acid and coumarin-3-carboxylic acid are found to be completely planar molecules at their most stable geometries, being in that respect similar to non-substituted cromone and coumarin. However, new structural features are brought into play by the –COOH substituents; indeed, these substituents allow for the occurrence of intramolecular hydrogen bonds involving the hydroxyl groups of the substituents and the oxygen atoms of the carbonyl groups. These interactions are in fact observed for these compounds since in both cases the hydrogen atom of the hydroxyl group points to the carbonyl oxygen atom resulting in O–H···O with included angles of about 150° and non-bonded O···H distances of 1.77 Å and 1.75 Å, respectively, for coumarin-3-carboxylic acid and chromone-3-carboxylic acid chromone-3-carboxylic acid. In both cases, these parameters have values which are characteristic of hydrogen bond formation (the van der Waals radius of oxygen atoms is about 1.46 Å). In addition those hydrogen bonds can be also characterized as resonance assisted hydrogen bonds (RAHB) [43–45] since their formation allows for another molecular ring to be closed.

Our experimental findings and also all our calculations predict coumarin-3-carboxylic acid to be more stable than chromone-3-carboxylic acid. Also all our calculations predict non-substituted coumarin to be more stable than non-substituted chromone, in which they agree with experimental observations [46]. Finally, both experimental and computational evidences suggest that the introduction of the –COOH substituents induces an attenuation of the stability difference between coumarin and chromone. Indeed, while experimentally coumarin is found to be 37.3 ± 4.1 kJ mol^{-1} more stable than chromone [46], coumarin-3-carboxylic acid is only 22.8 ± 4.2 kJ mol^{-1} more stable than chromone-3-carboxylic acid. This

Table 5 Derived standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation at $T = 298.15$ K

Compound	$-\Delta_f H_m^0$(cr)/kJ mol^{-1}	$\Delta_{cr}^{g} H_m^0$/kJ mol^{-1}	$-\Delta_f H_m^0$(g)/kJ mol^{-1}
Chromone-3-carboxylic acid	626.3 ± 2.3	113.8 ± 1.2	512.5 ± 2.6
Coumarin-3-carboxylic acid	653.5 ± 1.9	118.2 ± 2.7	535.3 ± 3.3

Table 6 DFT electronic energies, thermal corrections to $T = 298.15$ K, kJ·mol^{-1} and G3MP2 enthalpies at $T = 298.15$ K

Compound	$E_{\mathrm{B3LYP/6\text{-}311G^{**}}}$	$E_{\mathrm{B3LYP/cc\text{-}pVTZ}}$	$E_{\mathrm{MC\text{-}UT/3}}$	$E_{\mathrm{MC\text{-}QCISD/3}}$	H_{G3MP2}	$TCE_{\mathrm{B3LYP/6\text{-}31G^{*}}}$
Chromone-3-carboxylic acid	−685.78	−85.84	−684.74	−684.75	−684.62	0.14563
Coumarin-3-carboxylic acid	−685.79	−685.86	−684.75	−684.76	−684.63	0.14809
Chromone	−497.14	−497.19	−496.35	−496.36	−496.25	0.13109
Coumarin	−497.15	−497.21	−496.36	−496.37	−496.27	0.1307
1,4-Benzodioxan	−460.22	−460.27	−459.5	−459.51	−459.38	0.14806
1,4-Benzodioxan-2-carboxylic acid	−648.84	−648.91	−647.88	−647.89	−647.74	0.16478
Ethane	−79.857	−79.866	−79.713	−79.714	−79.647	0.07586
Propanoic acid	−268.49	−268.51	−268.1	−268.1	−268.01	0.09325

All energies are in a.u. (1 $E_{\mathrm{H}} = 2625.50184$ kJ mol^{-1})

$\mathrm{TCE}_{\mathrm{B3LYP/6\text{-}31G^{*}}} = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{zp}} + \Delta_{\mathrm{0K}}^{\mathrm{298.15K}} E_{\mathrm{vib}}$

Table 7 Nucleus Independent Chemical Shifts (ppm)

	Benzene ring		Pyranone ring	
	NICS(0)	NICS(1.0)	NICS(0)	NICS(1.0)
Benzene	−9.7	−11.5	–	–
Chromone	−10.27	−11.30	0.41	−3.12
Chromone-3-acid carboxylic	−10.07	−11.20	0.01	−3.42
Coumarin	−9.40	−10.69	−0.42	−3.24
Coumarin-3-acid carboxylic	−9.24	−10.72	−1.47	−4.10

attenuation closely parallels the corresponding one found from our more accurate (G3MP2) calculations, which predict stability differences of 39.8 kJ mol^{-1} and 32.0 kJ mol^{-1}, respectively, for the non-substituted and for the substituted systems. In order to clarify the influence of hydrogen bond formation in this behaviour we also conducted G3MP2 calculations for coumarin-3-carboxylic acid and chromone-3-carboxylic acid molecules constrained to conformations not allowing hydrogen bond formation, i.e. with the –OH fragments rotated 180° around the C–O bond. The resulting energy difference, 37.1 kJ mol^{-1}, is very close to the energy difference observed for the non-substituted molecules (i.e. almost no attenuation is observed) a fact which indicates that hydrogen bond formation must play an important role in the observed stability difference behaviour. Our NBO analyses suggest that the hydrogen bond strength is higher in chromone-3-carboxylic acid than in coumarin-3-carboxylic acid, as indicated by the stabilization resulting from the hyperconjugative interaction involving the carbonyl oxygen π lone-electronic pair (as donor) and the antibonding σ^{*} orbital of the –OH fragment (as acceptor), which amounts to 75.4 and to 63.9 kJ mol^{-1}, respectively, for chromone-3-carboxylic acid and for coumarin-3-carboxylic acid. Thus, according to our analysis, hydrogen bond formation involving the substituent and the carbonyl oxygen stabilizes more the chromone derivative than the coumarin one, thus leading to the observed equalization of the corresponding stabilities. Other important interactions analysed involve the π lone electronic pair of the oxygen atom of the pyranone ring and the σ^{*} antibonding orbital involving both atoms of the carbonyl group (C=O). These interactions, which only occur for

Table 8 Theoretical estimates of the standard enthalpies of formation in the gas phase at $T = 298.15$ K of chromone-3-carboxylic acid and chromone-3-carboxylic acid

Compound	R	$-\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}(\mathrm{g})$/kJ mol^{-1}					
		DFT/B3LYP		MC-UT/3	MC-QCISD/3	G3MP2	Exp.
		6-311G**	cc-pVTZ				
Chromone-3-carboxylic acid	IA	527.9	490.9	519.4	521.8	517.2	512.5 ± 2.6
	IB	533.5	497.6	523.0	525.1	524.0	
	At	408.2	429.1	493.8	501.6	518.4	
Coumarin-3-carboxylic acid	IIA	549.2	548.5	541.0	543.7	546.7	535.3 ± 3.3
	IIB	554.8	555.1	544.6	547.1	556.0	
	At	430.6	489.8	515.6	524.9	550.4	

At atomization reaction

the coumarin-based systems, are responsible for the greater stability of these systems, as described elsewhere [47]. Our NBO analysis indicate also an important role for this stabilizing interaction in explaining the relative stability of chromone-3-carboxylic acid and coumarin-3-carboxylic acid, since we observed it is attenuated by about 26 kJ mol^{-1} when we compare non-substituted coumarin and its 3-carboxylic acid [46].

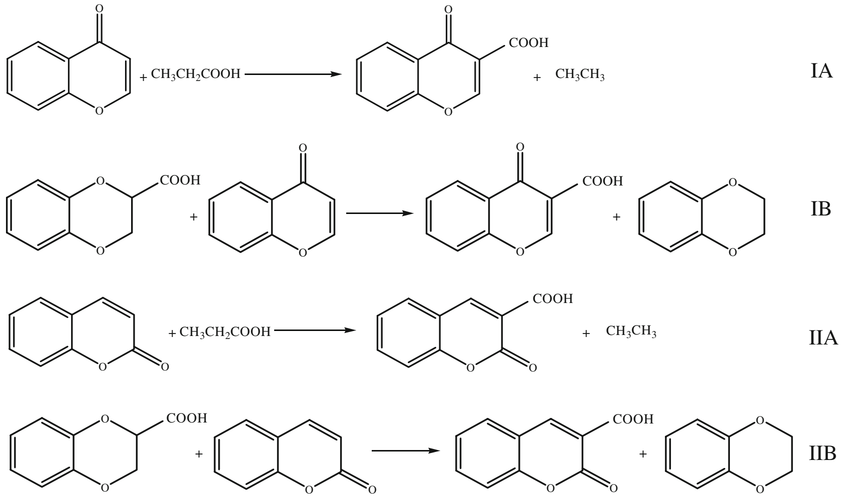
Thus both analysed interactions have the effect of attenuating the excess stability that coumarin based systems evidence when compared with chromone ones.

The NICS values calculated for both rings are reported in Table 7, where the values calculated for the non-substituted parent molecules and for benzene are also reported for comparison purposes; from these values we can observe that no remarkable effects of the introduction of the substituents are observed for the benzene rings, i.e. these rings preserve essentially their aromaticity upon substitution at the pyranone ring, while a small increasing effect is observed for the aromaticity of the pyranone ring. This effect can be attributed to the –COOH substituents which have π electron donor character, and thus enhance the π electronic density in the extended delocalized system.

Total energies, identified by the subscripts B3LYP/6-311G**, B3LYP/cc-pVTZ, MC-UT/3 and MC-QCISD/3 as well as thermal corrections, TCE/6-31G*, are reported in Table 6 for the studied compounds. We also report in that table the absolute enthalpies at 298.15 K, obtained from the G3MP2 calculations (in the column H_{G3MP2}).

In order to estimate the enthalpies of formation of the systems from the calculated energies we used the following set of isodesmic/homodesmic reactions involving auxiliary systems whose thermochemical properties are well established experimentally [42, 48, 49].

The optimum geometries, the energies and the thermal corrections for all the auxiliary molecules have also been obtained using the same procedures as described above.



The estimated values of molar enthalpies of formation in the gaseous phase obtained by DFT calculations and the more accurate MCCM and G3MP2 methods for the compounds are presented in Table 8, for all reactions used.

We can observe from that table that all levels of calculation provide estimates of the enthalpies of formation in reasonable agreement with experiment; however, only the most accurate calculations (MCCM and G3MP2 methods) can provide energies with enough accuracy so as to allow reliable use of atomization energies to estimate enthalpies of formation.

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References

1. Adeleke BB, Weir D, Depew MC, Wan JKS. An esr and CIDEP study of the photoreduction of chromone and chromanone and their organometallic adducts. Can J Chem. 1984;62:117–20.
2. Zhao P, Li J, Yang G. Synthesis and insecticidal activity of chromanone and chromone analogues of diacylhydrazines. Bioorg Med Chem. 2007;15:1888–95.
3. Cottiglia F, Dhanapal B, Sticher O, Heilmann J. New chromanone acids with antibacterial activity from *Calophyllum brasiliense*. J Nat Prod. 2004;67:537–41.

4. Aldrich. Handbook of Fine Chemicals and Laboratory Equipment. Madrid, Spain; 2004–2005.
5. Plato C, Glasgow AR Jr. Differential scanning calorimetry as a general method for determining purity and heat of fusion of high-purity organic chemicals. Application to 95 compounds. Anal Chem. 1969;41:330–6.
6. Sabbah R, Xu-wu A, Chickos JS, Leitão MLP, Roux MV, Torres LA. Reference materials for calorimetry and differential thermal analysis. Thermochim Acta. 1999;331:93–204.
7. Ribeiro da Silva MAV, Ribeiro da Silva MDMC, Pilcher G. The construction, calibration and use of a new high-precision static bomb calorimeter. Rev Port Quím. 1984;26:163–72.
8. Ribeiro da Silva MAV, Ribeiro da Silva MDMC, Pilcher G. Enthalpies of combustion of 1,2-dihydroxybenzene and of six alkylsubstituted 1,2-dihydroxybenzenes. J Chem Thermodyn. 1984;16:1149–55.
9. Santos LMNBF, Silva MT, Schröder B, Gomes L. Labtermo: methodologies for the calculation of the corrected temperature rise in isoperibol calorimetry. J Therm Anal Calorim. 2007;89: 175–80.
10. Coops J, Jessup RS, Van Nes K. Experimental thermochemistry: calibration of calorimeters for reactions in a bomb at constant volume. In: Rossini FD, editor. Interscience: New York; 1956. vol. 1, Chap. 3.
11. Wagman DD, Evans WH, Parker VB, Schumm RH, Halow I, Bailey SM, et al. The NBS tables of chemical thermodynamic properties. J Phys Chem Ref Data. 1982;11(Suppl 2).
12. Washburn EW. Standard states for bomb calorimetry. J Res Nat Bur Stand (US). 1933;10:525–58.
13. Hubbard WN, Scott DW, Waddington G. Experimental thermochemistry. In: Rossini FD, editor. Interscience: New York; 1956. vol. 1, Chap. 5.
14. Wieser ME. Atomic weights of the elements 2005 (IUPAC Technical Report). Pure Appl Chem. 2006;78:2051–66.
15. Adedeji FA, Brown DLS, Connor JA, Leung M, Paz-Andrade MI, Skinner HA. Thermochemistry of arene chromium tricarbonyls and the strengths of arene-chromium bonds. J Organomet Chem. 1975;97:221–8.
16. Chickos JS, Acree WE. Enthalpies of sublimation of organic and organometallic compounds. J Phys Chem Ref Data. 2002;31: 537–698.
17. Becke D. Density–functional thermochemistry. 3. The role of exact exchange. J Chem Phys. 1993;98:5648–52.
18. Lee T, Yang WT, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B. 1998;37:785–9.
19. Hariharan PC, Pople JA. The effects of d-functions on molecular orbital energies for hydrocarbons. Chem Phys Lett. 1972;66: 217–9.
20. Francl MM, Pietro WJ, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, et al. Self-consistent molecular orbital methods. XXIII. A polarization type basis set for second-row elements. J Chem Phys. 1982;77:3654–65.
21. Scott PA, Radom L. Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Moller-Plesset, quadratic configuration interaction, density functional theory and semiempiric scale factors. J Chem Phys. 1996;100:16502–13.
22. Hariharan PC, Pople JA. Influence of polarization functions on molecular-orbital hydrogenation energies. Theoret Chim Acta. 1973;28:213–22.
23. Frisch MJ, Pople JA, Binkley JS. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. J Chem Phys. 1884;80:3265–9.
24. Dunning TH Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J Chem Phys. 1989;90:1007–23.
25. Woon DE, Dunning TH Jr. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. J Chem Phys. 1993;98:1358–71.
26. Woon DE, Dunning TH Jr. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. J Chem Phys. 1994;100:2975–88.
27. Wilson AK, Woon DE, Peterson KA, Dunning TH Jr. Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton. J Chem Phys. 1999;110: 7667–76.
28. Lynch BJ, Truhlar DG. Robust and affordable multicoefficient methods for thermochemistry and thermochemical kinetics: the MCCM/3 suite and SAC/3. J Phys Chem A. 2003;107:3898–906.
29. Zhao Y, Lynch BJ, Truhlar DG. Multi-coefficient extrapolated density functional theory for thermochemistry and thermochemical kinetics. Phys Chem Chem Phys. 2005;7:43–52.
30. Curtiss LA, Redfern PC, Raghavachari K, Rassolov V, Pople JA. Gaussian-3 theory using reduced Møller-Plesset order. J Chem Phys. 1999;110:4703–9.
31. Reed E, Curtiss LA, Weinhold F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. Chem Rev. 1988;88:899–926.
32. Foster JP, Weinhold F. Natural hybrid orbitals. J Am Chem Soc. 1980;102:7211–8.
33. Reed E, Weinhold F. Natural bond orbital analysis of near-Hartree–Fock water dimer. J Chem Phys. 1983;78:4066–73.
34. GAMESS-UK is a package of ab initio programs written by Guest MF, van Lenthe JH, Kendrick J, Schoffel K, and Sherwood P, with contributions from Amos RD, Buenker RJ, van Dam HJJ, Dupuis M, Handy NC, Hillier IH, Knowles PJ, Bonacic-Koutecky V, von Niessen W, Harrison RJ, Rendell AP, Saunders VR, Stone AJ and de Vries AH. The package is derived from the originQMA_SOFT_VMMORAIS/dec_al GAMESS code due to Dupuis M, Spangler D and Wendoloski J, NRCC Software Catalog, vol. 1, Program No. QG01 (GAMESS); 1980.
35. The DFT module within GAMESS-UK was developed by Dr. P. Young under the auspices of EPSRC's Collaborative Computational Project No. 1 (CCP1) (1995–1997).
36. Zhao Y, Truhlar DG. MLGAUSS-version 2.0. Minneapolis: University of Minnesota; 2004.
37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, Revision C.02. Wallingford, CT: Gaussian, Inc.; 2004.
38. Schleyer PvR, Maerker C, Dransfeld A, Jiao H, Hommes NJRvE. Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. J Am Chem Soc. 1996;118:6317–8.
39. Glendening ED, Badenhoop JK, Reed AE, Carpenter JE, Bohmann JA, Morales CM, et al. NBO 5.0. Madison: Theoretical chemistry Institute, University of Wisconsin; 2001.
40. Rossini FD. Experimental thermochemistry: assignment of uncertainties to thermochemical data. In: Rossini FD, editor. Interscience: New York; 1956. vol. 1, Chap. 14.
41. CODATA. Recommended key values for thermodynamics, 1977. Report of the CODATA task group on key values for thermodynamics. J Chem Thermodyn. 1978;10:903–6.
42. Pedley JB. Thermochemical data and structures of organic compounds, vol. 1. College Station, Texas: TRC Data Series; 1994.
43. Bertolasi V, Gilli P, Ferretti V, Gilli G. Evidence for resonance-assisted hydrogen bonding. 2. Intercorrelation between crystal structure and spectroscopic parameters in eight intramolecularly hydrogen bonded 1,3-diaryl-1,3-propanedione enols. J Am Chem Soc. 1991;113:4917–25.
44. Wojtulewski S, Grabowski S. DFT and AIM studies on two-ring resonance assisted hydrogen bonds. J Mol Struct (THEOCHEM). 2003;621:285–91.

45. Matos MAR, Morais VMF, Ribeiro da Silva MDMC, Marques MCF, Sousa EA, Castñeiras JP, et al. Thermochemical and theoretical studies of dimethylpyridine-2,6-dicarboxylate and pyridine-2,3-, pyridine-2,5-, and pyridine-2,6-dicarboxylic acids. J Chem Eng Data. 2005;50:1184–91.
46. Matos MAR, Sousa CCS, Morais VMF, Liebman JF. Energetics of coumarin and chromone. J Phys Chem B. 2009;113:11216–21.
47. Matos MAR, Sousa CCS, Morais VMF. Experimental and computational thermochemistry of the isomers: chromanone, 3-isochromanone, and dihydrocoumarin. J Chem Thermodyn. 2009;41:308–14.
48. Matos MAR, Sousa CCS, Morais VMF. Experimental and computational thermochemistry of 1,4-benzodioxan and its 2-R derivatives. J Chem Thermodyn. 2008;40:1485–9.
49. Matos MAR, Sousa CCS, Morais VMF. Experimental and computational thermochemistry of 1,4-benzodioxan and its 6-R derivatives. J Phys Chem A. 2008;112:7961–8.