Energetics of 2- and 3-coumaranone isomers: A combined calorimetric and computational study

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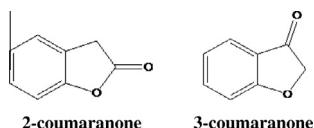
ARTICLE INFO

ABSTRACT

Condensed phase standard ($p° = 0.1$ MPa) molar enthalpies of formation for 2-coumaranone and 3-coumaranone were derived from the standard molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, measured by mini-bomb combustion calorimetry. Standard molar enthalpies of sublimation of both isomers were determined by Calvet microcalorimetry. These results were combined to derive the standard molar enthalpies of formation of the compounds, in gas phase, at $T = 298.15$ K. Additionally, accurate quantum chemical calculations have been performed using DFT methods and high level composite ab initio calculations. Theoretical estimates of the enthalpies of formation of the compounds are in good agreement with the experimental values thus supporting the predictions of the same parameters for isobenzofuranone, an isomer which has not been experimentally studied. The relative stability of these isomers has been evaluated by experimental and computational results. The importance of some stabilizing electronic intramolecular interactions has been studied and quantitatively evaluated through Natural Bonding Orbital (NBO) analysis of the wave functions and the nucleus independent chemical shift (NICS) of the studied systems have been calculated in order to study and establish the effect of electronic delocalization upon the relative stability of the isomers.

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1. Introduction

The compounds 2- and 3-coumaranone belong to a class of organic compounds named benzofuranones which present mutagenic and carcinogenic activity [1]. In spite of their rare natural occurrence [2], these compounds are readily synthesized and play an important role in the synthesis of many organic compounds [3,4]. In this work, we present a thermodynamic study of these two isomers, a comparison of their relative stabilities as well as a brief comparison with related compounds already studied by us [5].

2-coumaranone   **3-coumaranone**

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Enthalpies of combustion were determined by mini bomb calorimetry in order to derive the standard molar enthalpies of formation, in condensed phase at $T = 298.15$ K. The enthalpies of sublimation were obtained by Calvet microcalorimetry and the results were combined with those obtained by mini bomb calorimetry in order to derive the standard molar enthalpies of formation in gas phase at $T = 298.15$ K.

DFT/B3LYP calculations with extended basis set and high level ab initio calculations, G3MP2 and G3MP2B3, were performed and a high set of isodesmic reactions were used to predict the values of the enthalpies of formation in gas phase at $T = 298.15$ K. The results are in good agreement with experimental findings.

The relative stability of the two isomers was evaluated regarding experimental and theoretical results. Natural Bonding Orbital (NBO) analysis of the leading donor–acceptor interactions has been conducted using second-order perturbation theoretical techniques to evaluate the contribution of the electronic delocalization to the relative stability of the compounds.

The magnetic properties associated with the aromaticity/anti-aromaticity behaviour of the systems studied have also been assessed through the calculation and analysis of the nucleus independent chemical shift (NICS) tensors.

TABLE 1
Provinence and purity of the compounds studied.

Chemical name	CAS	Provenance	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
2-Coumaranone	553–86-6	Aldrich Chemical Co.	0.97	Sublimation	0.9998	GC–MS
3-Coumaranone	7169–34-8	Aldrich Chemical Co.	0.98	Sublimation	0.9994	GC–MS

This work is a contribution to a better understanding of some thermochemical properties of two benzofuranones and its relationship with their relative stability.

2. Experimental

2.1. Compounds and purity control

The two isomers studied were obtained commercially and purified by sublimation under reduced pressure. Details of the origin and purification of the samples are presented in table 1. The specific densities used to calculate the true mass were 1.2236 g · cm^{-3} for 2-coumaranone and 1.1936 g · cm^{-3} for 3-coumaranone.

2.2. Combustion calorimetry

Combustion experiments were performed in a mini-bomb combustion calorimeter (aneroid isoperibol calorimeter). A detailed description of the calorimetric system is found in literature [6] so, only a brief description of the main components and procedure will be given here. The mini-bomb is made of stainless steel with 18.185 cm^3 internal volume and electrodes and crucible support of platinum. The compounds were burned in a pellet form. In the case of 2-coumaranone the pellet was enclosed in Melinex bags, due to its high volatility, using the technique described by Skinner and Snelson [7], who determined the specific energy of combustion of dry Melinex as $\Delta_c u^0 = -(22902\ 5)$ J · g^{-1}. This value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported [7].

The platinum crucible containing the pellet and auxiliary material was placed in its support in the head of the mini-bomb with a 20 mm long platinum wire attached to each electrode terminal for electrical discharge and sample ignition. A platinum sheet was placed with an inverted "U shape" above the crucible to promote complete combustion. A total of 0.050 cm^3 of water was placed inside the body of the mini-bomb and the head with a Viton O-ring was then tightly adjusted to it by means of a stainless steel screwring. The bomb was filled three-times with ultra-pure oxygen and purged before being filled with 3.04 MPa. Afterwards, the bomb was introduced into a cylindrical copper block. The block was sealed, evacuated and filled with ultra-pure helium up to 0.2 MPa. This copper block is confined within a cylindrical cavity surrounded by a 9 dm^3 thermostatic water bath, regulated at constant temperature $T = (298.420 \pm 0.001)$ K by a TRONAC temperature controller (model PTC-40). A multimeter (Keithley, model 2000) interfaced to a PC was used for data acquisition containing a bean type thermistor ($R = 4$ K at $T = 298.15$ K) for temperature measurement. The charging, firing circuit and voltage measurement across the 2000 lF discharger condenser were done automatically by means of a set of Advantech acquisition/automation modulus, series 4000. At the end of the combustion experiment, the bomb was depressurized and the amount of carbon soot, when formed, was determined by gravimetry. The electrical energy for ignition, ΔUign, 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,

$$\Delta U(IBP) = -\mu_{cal} \cdot \Delta T_{ad} + \varepsilon_i \cdot (T_i - 298.15) + \varepsilon_f \cdot (298.15 - ''T_{ad} - T_i) + \Delta U\text{ign}, \quad (1)$$

where $\Delta U(IBP)$ is the energy associated with the isothermal bomb process, ε_i and ε_f are the energy of the bomb contents before and after ignition, respectively and ΔT_{ad} the adiabatic temperature obtained by application of the Regnault–Pfaundler method in a modified version of the LABTERMO software [8].

The energy equivalent of the mini-bomb combustion calorimeter, $e_{cal} = (1946.71 \pm 0.84)$ J · K^{-1}, was obtained from the calibration experiments, made with benzoic acid (NIST SRM 39j) with a certified massic energy of combustion of $-(26434 \pm 3)$ J · g^{-1} under bomb conditions. The atomic mass of the elements were those recommended by the IUPAC Commission in 2007 [9].

2.3. Calvet microcalorimetry

The standard molar enthalpies of sublimation of the two isomers were measured using the "vacuum sublimation" drop microcalorimetric technique [10,11]. The apparatus and technique have been described [11]. Samples about 3–8 mg in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot vessel in a high-temperature Calvet microcalorimeter held at $T = 319$ K for 2-coumaranone and at $T = 370$ K for 3-coumaranone, and then removed from the hot zone by vacuum sublimation or vaporization. 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. The microcalorimeter (Calvet High Temperature Microcalorimeter, SETARAM HT 1000) was calibrated in situ for these measurements using the reported standard molar enthalpies of sublimation of naphthalene [12].

From six independent experiments we have obtained a mean value for the observed standard molar enthalpies of sublimation, $\Delta_{cr,298.15K}^{g,T} H_m^0$, which was then corrected to $T = 298.15$ K, $\Delta_{298.15K}^{T} H_m^0(g)$, using the equation:

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

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(d) basis set.

2-Coumaranone

$$C_{p,m}^0(g)/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -0.000192(T/\text{K})^2 + 0.011(T/\text{K}) - 20.508. \quad (3)$$

3-Coumaranone

$$C_{p,m}^0(g)/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -0.000191(T/\text{K})^2 + 0.012(T/\text{K}) - 20,616. \quad (4)$$

3. Computational details

The optimum geometries of all molecules have been determined using density functional theory (DFT) with the Becke

three-parameter hybrid exchange [13] and the Lee–Yang–Parr [14] correlation functionals (B3LYP) together with the 6–31G(d) basis set [15,16]. The optimum structures so obtained have further been confirmed as true minima by constructing and diagonalizing the corresponding Hessian matrices, a procedure that also provides reliable estimates of the harmonic vibrational frequencies which, after being properly scaled by the recommended factor of 0.9614 [17], allows the estimations of the molecular thermal corrections needed to obtain molecular energies and enthalpies at any temperature. These structures also served as the reference structures to more accurate single-point energy calculations we further carried out, namely at the DFT/B3LYP level with the 6-311 + G(2d,p) and 6-311 + G(2df,2p) [18].

Additionally we have performed G3-based quantum chemistry calculations: G3(MP2) and G3(MP2)B3. G3 methods are based on *ab initio* molecular orbital theory and uses geometries obtained from second-order perturbation theory, MP2/6-31G(d), and zero-point energies from Hartree–Fock theory, HF/6-31G(d), followed by a series of single-point energy calculations. In G3 (MP2) the basis set extensions are obtained at the MP2 level [19], the G3(MP2)B3 corresponds to a modification of G3(MP2) to use B3LYP/6-31G(d) geometries and zero-point energies [20]. 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 co-workers as a means of providing useful aromaticity indices [21]. 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 non-weighted mean of the homologous coordinates of the heavy atoms of the rings), denoted NICS(0), and 1.0 Å above the centre of the ring, denoted NICS(1.0).

All calculations, including the geometry optimizations, vibrational analysis, single point calculations and the magnetic properties (NICS) calculations have been performed using the Gaussian 03 series of programs [22]. The NBO analysis of the wave functions has been performed with the NBO 5 program [23] incorporated in the Gaussian 03 package. Unless otherwise stated the experimental enthalpies of formation of all auxiliary compounds are taken from the Pedley's compendium [24].

4. Results

4.1. Experimental

In table 2 we present typical results of the combustion experiments for both isomers. The standard massic energy of combustion, $\Delta_c u^0$, calculated for both compounds corresponds to the combustion reaction according to the following chemical equation:

$$C_8H_6O_2(cr) + 17/2O_2(g)8CO_2(g) + 3H_2O(l). \tag{5}$$
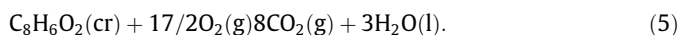
The energy corrections to the standard state, ΔU_Σ, of the intervening species, were calculated following the procedure indicated by Hubbard *et al.*[25]. Table 3 lists the individual values for the combustion experiments and table 4 shows the derived standard molar energies and enthalpies of combustion, $\Delta_c U_m^0(cr)$ and $\Delta_c H_m^0(cr)$, and the standard molar enthalpies of formation in the crystalline phase, $\Delta_f H_m^0(cr)$, at $T = 298.15$ K. In accordance with customary thermochemical practice [26], the uncertainty assigned to the standard molar enthalpies of combustion is twice the overall standard deviation of the mean and includes the uncertainties in calibration and in the values of auxiliary quantities used. In order to derive $\Delta_f H_m^0(cr)$ from $\Delta_c H_m^0(cr)$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$, at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ $\cdot$ mol^{-1}[27] and $-(393.51 \pm 0.13)$ kJ $\cdot$ mol^{-1}[27], respectively, were used.

TABLE 2
Typical combustion experiments, at $T = 298.15$ K.

	2-Coumaranone	3-Coumaranone
m (cpd)/mg	19.5526	22.1858
m (Melinex)/mg	0.9151	
T_i/K	298.1486	298.1489
T_f/K	298.5195	298.4654
ΔT_{ad}/K	0.38616	0.31910
ε_{cal}/(J $\cdot$ K^{-1})	1946.71	1946.71
ε_i/(J $\cdot$ K^{-1})	0.7859	0.7780
ε_f/(J $\cdot$ K^{-1})	0.8156	0.8023
$-\Delta U$(IBP)/J	750.0657	619.6943
ΔU(Melinex)/J	209.58	
ΔU(ign.)/J	1.00	0.88
ΔU(carb)/J	0.18	0
ΔU_Σ/J	0.5538	0.4271
$-\Delta_c u^0$/(J $\cdot$ g^{-1})	27674.95	27952.49

m(cpd) is the mass of compound burnt in the experiment; m(fuse) is the mass of fuse (cotton) used in the experiment and m(Melinex) is the mass of Melinex used in the 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; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(IBP) includes the ignition energy, ΔU(ignition) and ΔU(Melinex) is the energy of combustion of Melinex; ΔU(carbon) is the energy correction for carbon formation; $\Delta U\Sigma$ is the energy correction to the standard state; $\Delta_c u^\circ$ is the standard massic energy of combustion.

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

$-\Delta_c u^0$/(J $\cdot$ g^{-1})	
2-Coumaranone	3-Coumaranone
27685.56	27957.85
27674.95	27961.21
27662.13	27951.76
27680.98	27952.49
27674.15	27959.61
27663.58	27935.80
$-\Delta_c u^0$/(J $\cdot$ g^{-1})	
27673.6 ± 3.8	27953.1 ± 3.8

The standard molar enthalpies of sublimation were obtained from at least six independent microcalorimetric experiments. The uncertainty of the results is twice the standard deviation of the mean. These results are summarized in table 5. From the values for the standard molar enthalpies of formation and sublimation of the crystalline compounds, the value of the standard molar enthalpies in the gaseous phase was derived.

4.2. Computational results and discussion

Each of the three isomeric benzofuranones studied has an optimum geometry consisting of a planar benzenic ring fused to a heterocyclic ring which also assumes a perfectly planar conformation. This particular conformation allows possible electron delocalization interactions involving both rings, thus eventually leading to further stabilization of the isomers.

Energetically, both our calculations and our experimental findings predict 2-coumaranone to be considerably (*ca.* 44.5 ± 4.9 kJ $\cdot$ mol^{-1} and 55.7 kJ $\cdot$ mol^{-1} on the experimental and computational sides, respectively) more stable than 3-coumaranone. Previously, we observed a similar stability ordering behaviour for other related species isomeric pairs: coumarin has been found to be more stable than chromone (by about 37.3 ± 4.1 kJ $\cdot$ mol^{-1}) [28] while dihydrocoumarin was observed to be more stable than its isomeric chromanone (by about (43.4 ± 3.3) kJ $\cdot$ mol^{-1}) [29]. In both cases the extra stability has

TABLE 4
Derived standard ($p°$ = 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})
2-Coumaranone	3712.0 3.5	3713.2 3.5	292.4 3.7
3-Coumaranone	3749.5 1.7	3750.7 1.7	254.9 2.0

TABLE 5
Derived standard ($p°$ = 0.1 MPa) molar enthalpies of formation, at T = 298.15 K, of the two isomers.

Compound	$-\Delta_f H_m^0$ (cr) (kJ · mol^{-1})	$\Delta_{cr}^g H_m^0$ (kJ · mol^{-1})	$-\Delta_f H_m^0$ (kJ · mol^{-1})
2-Coumaranone	292.4 3.7	78.7 1.7	213.6 4.1
3-Coumaranone	254.9 2.0	85.8 1.7	169.1 2.6

TABLE 6
Electronic energies, absolute enthalpies and thermal corrections to T = 298.15 K (all values in Hartree[a], E_h).

Compound	$E_{B3LYP/6-31G(d)}$/ Hartree	$E_{B3LYP/6-311+G(2d,p)}$/ Hartree	$E_{B3LYP/6-311+G(2df,2p)}$/ Hartree	$H_{G3(MP2)//B3LYP}$/ Hartree	$H_{G3(MP2)}$/ Hartree	[b]$TCE_{B3LYP/6-31G(d)}$/ Hartree
2-Coumaranone	−458.921263	−459.059463	−459.076312	−458.245197	−458.225975	0.129819
3-Coumaranone	−458.903031	−459.041495	−459.058103	−458.223979	−458.204712	0.129997
Isobenzofuran-1(3H)-one	−458.922748	−459.061362	−459.078045	−458.245879	−458.226524	0.130638
Methane	−40.518389	−40.534896	−40.536948	−40.420556	−40.418284	0.049030
Water	−76.408953	−76.459526	−76.462564	−76.341865	−76.338625	0.024946
Ethene	−78.587458	−78.617640	−78.621098	−78.434971	−78.430763	0.055214
Ethane	−79.830418	−79.858377	−79.861748	−79.651021	−79.646717	0.070651
Formaldehyde	−114.500472	−114.544267	−114.547938	−114.354201	−114.349218	0.030644
Methanol	−115.714407	−115.767617	−115.771999	−115.553223	−115.547926	0.055711
Butane	−158.458041	−158.509047	−158.515200	−158.120740	−158.112435	0.139556
Cyclopentane	−196.557075	−196.616107	−196.623081	−196.162611	−196.153445	0.147543
3,4-Dihydro-2H-pyrrole	−211.372248	−211.436558	−211.443649	−211.003289	−210.992694	0.111303
Tetrahydrofurane	−232.449443	−232.524655	−232.532909	−232.061157	−232.050200	0.123272
Cyclopentanone	−270.572827	−270.658858	−270.667772	−270.127407	−270.114973	0.128364
2-Tetrahydrofuranone	−306.492613	−306.593176	−306.603544	−306.051619	−306.038638	0.105151
1,3-Dioxolan-2-one	−342.398474	−342.513354	−342.525369	−341.963287	−341.949505	0.081220
Tetrahydro-2H-pyran-2-one	−345.803532	−345.915195	−345.927064	−345.283617	−345.268664	0.135368
Indane	−348.988153	−349.085658	−349.098895	−348.359711	−348.343286	0.172899
Benzoxazole	−399.723232	−399.839328	−399.854577	−399.122777	−399.105833	0.112874
Dihydro-2,5-furandione	−380.523074	−380.649276	−380.661773	−380.030543	−380.015185	0.086166
2,3-Dihydrobenzofurane	−384.883724	−384.996704	−385.011373	−384.259605	−384.242623	0.148561
Benzodioxole	−420.777089	−420.904820	−420.921058	−420.158547	−420.141234	0.123948
2-Indanone	−423.001257	−423.125438	−423.140643	−422.321071	−422.302221	0.153631
1-Indanone	−423.008167	−423.131670	−423.146773	−422.325249	−422.306498	0.154474
Chromone	−497.023203	−497.170582	−497.189282	−496.270966	−496.250239	0.136618
Coumarin	−497.023718	−497.171816	−497.190479	−496.286114	−496.265407	0.136340
Chroman-4-one	−498.222008	−498.360200	−498.378072	−497.465066	−497.443890	0.160539
Phthalic anhydride	−532.952053	−533.114919	−533.133703	−532.222425	−532.200876	0.112132
Dihydrocoumarin	−498.237133	−498.386342	−498.404577	−497.482714	−497.461623	0.160309

[a] Atomic unit of energy Hartree: 1 E_h = 2625.50184 kJ · mol^{-1}.
[b] $TCE_{B3LYP/6-31G(d)}$ = E_{trans} + E_{rot} + E_{ZP} + $D_{OK}^{298.15K} E_{vib}$

been attributed to the presence of the $-O-C=O$ fragment, which has considerable stabilization energy, identified as resonance energy and comparable to that of $N-C=O$, the highly stabilized amide group [30]. So, the presence of the $-O-C=O$, can again, hopefully, be invoked to explain the observed stability order within the 2-coumaranone and 3-coumaranone set of isomeric molecules.

The similarity between the pair 2-coumaranone/3-coumaranone and dihydrocoumarin/chromanone is remarkable and supports the plausibility of the common origin of the stabilizing effects. The enhanced stability afforded by the $-O-C=O$ fragment can be phenomenologically associated with the possibility of involvement of the lone-electronic pairs of both oxygen atoms in conjugative or hyperconjugative mutual interactions, these being especially important when this fragment can directly interact with the contiguous aromatic ring, thus enhancing the extended electronic delocalization occurring therein.

Quantitatively, we can probe the effects of the interactions involving electron delocalization of the lone electronic pairs of the oxygen atoms through an analysis of the wave functions in the framework of Natural Bond Orbital (NBO) theory [23,31–33], according to which, the electronic population should be distributed over a set of localized one-centre ("lone-pair") and two-centre ("bond") orbitals closely mimicking a classical Lewis-type description of the electronic system. Within this view, delocalization effects are evidenced by small occupancies of the set of antibonding orbitals. The stabilizing effect of such delocalization interactions can be quantitatively obtained as second-order perturbative estimates of the corresponding bonding–anti-bonding interactions. Such procedure lead us to identify the leading donor–acceptor interactions which are responsible for the different stabilities of the coumaranones as being those involving the π lone electronic-pair of the ring oxygen and the anti bonding $\pi^*_{C=O}$ orbi-

TABLE 7
Calculated estimates of the standard enthalpies of formation in the gas phase at T = 298.15 K for 2- and 3-coumaranone.

Molecule	Reaction	$-\Delta_f H_m^0(g)/kJ \cdot mol^{-1}$				
		DFT/B3LYP			Composite	
		6-31G(d)	6-311+G(2d,p)	6-311+G(2df,2p)	G3(MP2)//B3LYP	G3(MP2)
2-Coumaranone	IA	209.8	209.5	209.7	216.0	215.4
	IIA	212.4	207.7	208.3	222.1	224.8
	IIIA	211.2	208.9	209.3	213.1	212.2
	IVA	220.1	226.3	226.3	217.8	215.3
	VA	212.5	215.1	215.6	213.3	213.2
	VIA	222.6	224.4	224.9	225.0	225.8
	VIIA	203,9	204,9	204,3	210.0	211.1
	VIIIA	222.5	222.5	222.5	220.3	220.0
	IXA	226.5	224.6	224.8	218.9	218.8
	BSR	203.4	181.6	188.9	218.3	224.3
	Average	214.5	212.6	213.5	217.5	218.1
3-Coumaranone	IB	161.5	161.9	161.4	160.3	159.6
	IIB	164.0	160.0	160.0	166.4	169.0
	IIIB	162.8	161.3	161.0	162.6	161.6
	IVB	171.8	178.6	178.0	162.1	159.5
	VB	164.2	167.5	167.3	157.6	157.3
	VIB	174.3	176.8	176.6	169.3	170.0
	VIIB	155,6	157,3	156,1	155.4	154.2
	VIIIB	174.2	174.2	174.2	164.6	164.2
	IXB	169.7	170.2	170.1	159.6	159.2
	BSR	155.6	134.4	141.1	162.6	168.4
	Average	165.4	164.2	164.6	162.1	162.3

TABLE 8
Calculated estimates of the standard enthalpies of formation in the gas phase at T = 298.15 K for isobenzofuran-1(3H)-one.

Molecule	Reaction	$-\Delta_f H_m^0(g)/kJ \cdot mol^{-1}$	
		G3(MP2)//B3LYP	G3(MP2)
Isobenzofuranone	I	221.1	221.2
	II	227.2	230.6
	III	220.1	218.9
	IV	219.6	216.7
	V	215.1	214.6
	VI	226.8	227.2
	VII	211.4	210.0
	VIII	222.1	221.5
	BSR	220.1	225.7
	Average	220.4	220.7

tal, contributing with a stabilization energy of about 213 kJ · mol^{-1}, as well as the interaction involving the π lone electronic-pair of the carbonyl oxygen atom and the ring anti-bonding σ^*_{C-O} orbital, which contributes with a stabilization energy of about 222 kJ · mol^{-1}. We must stress that while none of these interactions is allowed to occur in 3-coumaranone, both are allowed to occur in isobenzofuranone where they contribute with about 234 kJ · mol^{-1} and 213 kJ · mol^{-1}, respectively. For 3-coumaranone a stabilizing interaction occurs involving the benzenic ring double-bond which is closest to the five-membered ring and the anti-bonding $\pi^*_{C=O}$ orbital; this stabilizing interaction contributes with about 167 kJ · mol^{-1}. This interaction is also allowed in isobenzofuranone where it affords stabilization of about 129 kJ · mol^{-1}. Thus, according to this simple NBO analysis, donor acceptor interactions favour stabilization of 2-coumaranone and isobenzofuranone over stabilization of 3-coumaranone, as we indeed observed from the experimental data and from the accurate quantum chemical calculations. In addition, isobenzofuranone is predicted to be slightly more stable than 2-coumaranone, which is indeed observed from our accurate calculations, as we will see latter.

The eventual aromatic behaviour of each ring in the studied systems can be probed through the calculation and analysis of the nucleus independent chemical shifts (NICS). For 2-Coumaranone the

NICS values calculated from the RHF/6-311G∗∗ wave function are as follows (all values in 10^{-6} units): $\sigma_{iso}(0) = -0.7$, $\sigma_{ZZ}(0) = +26.4$, $\sigma_{iso}(1) = -2.1$, $\sigma_{ZZ}(1) = -0.4$ (5-membered ring) and $\sigma_{iso}(0) = -11.3$, $\sigma_{ZZ}(0) = -15.2$, $\sigma_{iso}(1) = -12.0$, $\sigma_{ZZ}(1) = -30.0$ (6-membered ring), while, for 3-coumaranone we found the values: $\sigma_{iso}(0) = +0.5$, $\sigma_{ZZ}(0) = +22.6$, $\sigma_{iso}(1) = -2.2$, $\sigma_{ZZ}(1) = -2.0$ (5-membered ring) and $\sigma_{iso}(0) = -10.3$, $\sigma_{ZZ}(0) = -12.3$, $\sigma_{iso}(1) = -11.4$, $\sigma_{ZZ}(1) = -27.9$ (6-membered ring) and for Isobenzofuranone: $\sigma_{iso}(0) = -3.1$, $\sigma_{ZZ}(0) = +20.9$, $\sigma_{iso}(1) = -3.4$, $\sigma_{ZZ}(1) = -3.6$ (5 membered ring) and $\sigma_{iso}(0) = -10.5$, $\sigma_{ZZ}(0) = -14.7$, $\sigma_{iso}(1) = -12.3$, $\sigma_{ZZ}(1) = -31.0$ (6-membered ring), Thus, we can observe that, while the aromaticity of the six-membered rings is clearly unquestionable for all isomers, the five-membered rings are non-aromatic in nature, as expected. According to the magnetic parameters analysis, non-aromaticity or, at most, a very mild aromatic character should perhaps be associated to the five-membered rings. Indeed, we can observe that both the isotropic and the out-of-plane components of the chemical shielding tensor measured 0.10 nm above the ring geometric centre are slightly negative, the most negative corresponding to isobenzofuranone, which is in agreement with our previous prediction.

Even the most accurately calculated energies are always affected by inherent errors mainly associated with a deficient description of electron correlation. As such, the conversion of such energies into meaningful molecular thermochemical parameters requires the use of chemical schemes which can, hopefully, ensure a maximal cancellation of those errors, between the reactants and the products side. Such chemical schemes must involve the maximum possible degree of bond pattern similarity between reactants and products and, at the same time, use only molecular species which have been accurately characterized from the experimental thermochemistry viewpoint. By adopting such convenient schemes, we thus hope to be able to estimate accurately their enthalpy variation and, ultimately, to get reliable estimates of the unknown standard enthalpies of formation. A detailed analysis of the thermochemical literature led us to consider the following set of isodesmic/homodesmotic reactional schemes, exemplified here for 2-coumaranone only:
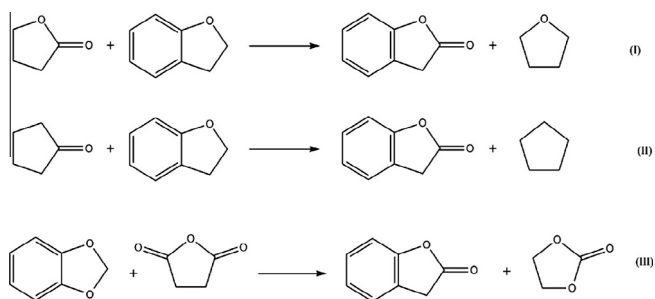
Additionally, the following homodesmotic reactional schemes using different reactants (2-indanone or 3-indanone) are also considered:
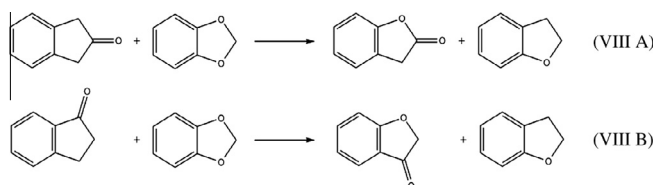
The calculated electronic energies and absolute enthalpies at T = 298.15 K, for the isomers studied as well as for all the auxiliary molecules involved in the isodesmic/homodesmotic reactions are shown in table 6, while the corresponding estimated standard enthalpies of formation are reported in tables 7 and 8.

It can be informative to consider also the following homodesmotic reaction,
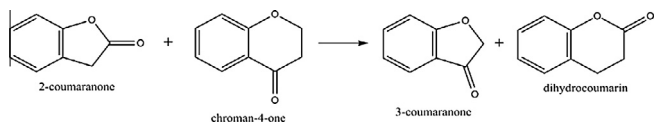
which is observed to be thermoneutral (the experimental enthalpy variation is (1.1 to 5.9) kJ · mol^{-1}, and is also very well described by our calculations (9.3 and 9.4) kJ · mol^{-1}, respectively, from the G3(MP2) and G3(MP2)//B3LYP calculations), and compare it with the similar homodesmotic reaction involving the more unsaturated chromone/coumarin isomeric pair:

This reaction is observed experimentally to be unequivocally endothermic by (7.2 to 6.4) kJ · mol^{-1}, an observation also corroborated by our accurate calculations: (16.0 and 15.9) kJ · mol^{-1} from the G3(MP2) and G3(MP2)//B3LYP calculations. The different thermal behaviour of both reactions can be associated with the possibility of a persistent residual interaction involving the π-lone electronic pairs of the ring oxygen and of the carbonyl oxygen atom allowed by the intercalation of a double C=C bond between both groups in chromone. This effect is not allowed in chroman-4-one and is not also allowed in 3-coumaranone, of course and helps rationalizing the observed isomerisation enthalpies involving the several iso-

meric molecular pairs; in fact, we observe that, according to the isomerisation enthalpies, the pair 2-coumaranone/3-coumaranone with isomerisation enthalpy from (44.5 to 4.9) kJ · mol^{-1} is much closer to the pair dihydrocoumarine/chromanone (43.4 ± 3.3) kJ · mol^{-1} than to the pair coumarine/chromone (37.3 ± 4.1) kJ · mol^{-1}. In other words, we observe that the stabilization of 2-coumaranone as compared to 3-coumaranone is closer to the corresponding stabilization of dihydrocoumarine relative to chromone than that observed for the pair coumarin/chromone. The reason has been pointed out earlier resulting from a residual interaction between the π-lone pairs of the ring oxygen atom and those of the carbonyl group facilitated by the intercalation of a double bond between both groups in chromone.

Finally, we would like to corroborate further the quality of our estimates of the standard enthalpy of formation of isobenzofuranone reported in table 7, which show a large degree of mutual coherence, the two average values obtained agreeing with each other to within about 0.3 kJ · mol^{-1}. To do so, we will consider the homodesmotic reaction converting isobenzofuranone into methyl benzoate and involving also methane and ethane, as auxiliary molecular species. This reaction is predicted to be endothermic by 15.40 kJ · mol^{-1} from the G3(MP2) calculations, a value which agrees closely with the value (9.6 ± 4.0) kJ · mol^{-1} obtained by using our estimated G3(MP2) enthalpy of formation for iso-benzofuranone as well as the experimental values for methane and ethane and the recently recommended value for methyl benzoate, $-(276.1 ± 4.0)$ kJ · mol^{-1}[34]. This observation thus contributes to emphasize the reliability of our recommended estimate of the enthalpy of formation of isobenzofuranone."

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JCT 13-420