



## Experimental and computational thermochemistry of 6,7-dihydro-4(5H)-benzofuranone

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### ARTICLE INFO

#### Article history:

Received 23 April 2012

Received in revised form 4 July 2012

Accepted 5 July 2012

Available online 21 July 2012

#### Keywords:

Benzofuranone

Enthalpy of formation

Calorimetry

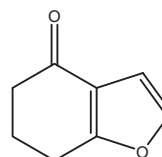
Computational calculations

DFT

G3(MP2) and G3(MP2)//B3LYP

### ABSTRACT

The standard ( $p = 0.1$  MPa) molar enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone was measured, at  $T = 298.15$  K, by static bomb calorimetry and the standard molar enthalpy of vaporization, at  $T = 298.15$  K, was obtained using Calvet microcalorimetry. These values were combined together to derive the standard molar enthalpy of formation of the title compound in gaseous phase, at  $T = 298.15$  K,  $-(226.0 \pm 2.8)$  kJ  $\cdot$  mol<sup>-1</sup>.



Additionally, density functional theoretical calculations using the B3LYP hybrid exchange-correlation energy functional with extended basis sets and also other higher-level *ab initio* quantum calculations have been performed.

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## 1. Introduction

Heterocyclic compounds probably constitute the largest and most varied family of organic compounds. Having a natural or synthetic origin these compounds play an important role in many areas of knowledge. Following our previous work with heterocyclic compounds [1–5], we present here a thermochemical study of 6,7-dihydro-4(5H)-benzofuranone. Benzofuranone derivatives show many different properties from antioxidant [6] to antibacterial activity against both Gram positive and Gram negative bacteria [7].

In this work, we report the experimental values of the enthalpy of formation, in the condensed phase of 6,7-dihydro-4(5H)-benzofuranone obtained by static bomb calorimetry, of the enthalpy of vaporization measured by Calvet microcalorimetry, and of the derived standard molar enthalpy of formation, in gas phase. We also report the performed density functional theory calculations and

high-level *ab initio* calculations namely, G3(MP2) and G3(MP2)//B3LYP.

## 2. Experimental

### 2.1. Materials and purity control

The 6,7-dihydro-4(5H)-benzofuranone [16806-93-2] was obtained from Aldrich Chemical Co. at a stated mass fraction purity of 0.980 and was purified further by distillation. Gas liquid chromatography analysis (Agilent 4890 D Chromatographer) was performed for the purchased compound (a pasty solid) and for the purified compound, which was in the liquid state, at ambient temperature. The purity of the liquid obtained was evaluated as mass fraction 0.9992. The purity of the sample was also confirmed through the carbon dioxide recovery ratio. The average ratio, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample was  $(0.9996 \pm 0.003)$ . The density of the sample is  $1.162$  g  $\cdot$  cm<sup>-3</sup> [8].

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## 2.2. Experimental determination of the enthalpy of formation in the gas phase

The enthalpy of formation of 6,7-dihydro-4(5*H*)-benzofuranone in the gas phase,  $\Delta_f H_m^0(\text{g})$ , at  $T = 298.15$  K, was determined combining the experimental values of the standard enthalpy of formation in the condensed state,  $\Delta_f H_m^0(\text{l})$ , and of the standard phase change enthalpy,  $\Delta_g^s H_m^0$ .

### 2.2.1. Combustion calorimetry

The standard molar enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone in the condensed phase was obtained from combustion calorimetry with a static bomb calorimeter. The apparatus and technique have been described previously [9,10]. Benzoic acid (NBS thermochemical standard 39j) was used for calibration of the bomb. Its massic energy of combustion is  $\Delta_c u^0 = -(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ , under certificate conditions. The calibration results were corrected to give the energy equivalent  $\varepsilon_{\text{cal}}$  corresponding to the average mass of water added to the calorimeter, 3119.6 g. From six independent calibration experiments performed  $\varepsilon_{\text{cal}} = (15995.3 \pm 2.0) \text{ J} \cdot \text{K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean.

Samples of 6,7-dihydro-4(5H)-benzofuranone were enclosed in polyester bags made of Melinex<sup>®</sup>, using the technique described by Skinner and Snelson [11] who determined the specific energy of combustion of dry Melinex<sup>®</sup> as  $\Delta_c u^0 = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ ; 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 [11]. Additionally, *n*-hexadecane (Aldrich Gold Label, mass fraction > 0.999) stored under nitrogen was used as auxiliary combustion aid, and its mass-specific energy of combustion was measured in our laboratory as  $-(47126.0 \pm 4.1) \text{ J} \cdot \text{g}^{-1}$ .

Combustion experiments were made in oxygen at  $p = 3.04$  MPa, with  $1.00 \text{ cm}^3$  of water added to the bomb:  $\Delta U_{\Sigma}$  is the correction to the standard state. For the cotton-thread fuse, empirical formula  $\text{CH}_{1.686}\text{O}_{0.843}$ ,  $\Delta_c u^0 = -16250 \text{ J} \cdot \text{g}^{-1}$  [12]; this value has been confirmed in our laboratory. The corrections for nitric acid formation  $\Delta U(\text{HNO}_3)$  were based on  $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$  [13] for the molar energy of formation of  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HNO}_3(\text{aq})$  from  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}(\text{l})$ . The mass of 6,7-dihydro-4(5H)-benzofuranone,  $m(\text{compound})$ , used in each experiment was determined from the total mass of carbon dioxide,  $m(\text{CO}_2, \text{total})$ , produced after allowance for that formed from the cotton thread fuse, Melinex and from the combustion auxiliary, *n*-hexadecane. An estimated pressure

coefficient of specific energy:  $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$  at  $T = 298.15 \text{ K}$ , a typical value for most organic compounds, was assumed [14]. As samples were ignited at  $T = 298.15 \text{ K}$ , the energy associated to the isothermal bomb process,  $\Delta U(\text{IBP})$ , was calculated using the following expression:

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

where  $\Delta m(\text{H}_2\text{O})$  is the difference between the mass of water in the calorimeter used in each experiment and that one (3119.6 g) to which  $\varepsilon_{\text{cal}}$  is referred;  $c_p(\text{H}_2\text{O}, \text{l})$  is the value of heat capacity of water,  $\varepsilon_f$  is the energy of the bomb contents after ignition and  $\Delta T_{\text{ad}}$  is the adiabatic temperature raise calculated using the program LABTERMO [15]. The atomic weights of the elements are those recommended by the IUPAC commission in 2007 [16].

### 2.2.2. Microcalorimetry Calvet

The standard molar enthalpy of vaporization of 6,7-dihydro-4(5H)-benzofuranone was measured using the “vacuum sublimation” drop microcalorimetric technique [17,18]. The apparatus and technique have been described [18]. 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  $T = 360$  K, and then removed from the hot zone by vacuum 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 enthalpy of vaporization of *n*-undecane [19].

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

$$\Delta_{98.15K}^T H_m^0(g) = \int_{298.15K}^T C_{p,m}^0(g) dT, \quad (2)$$

where  $T$  is the temperature of the hot reaction vessel,  $C_{p,m}^0(\text{g})$  is the molar heat capacity of 6,7-dihydro-4(5*H*)-benzofuranone in the gas phase which 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:

$$C_{p,m}^0(\text{g})/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = -0.000318(T/\text{K})^2 + 0.669(T/\text{K}) - 38.635. \quad (3)$$

**TABLE 1**  
Standard ( $p^0 = 0.1$  MPa) massic energy of combustion of 6,7-dihydro-4(5H)-benzofuranone at  $T = 298.15$  K.

[illegible]

### 3. Computational details

The geometries of all molecules used in this work were obtained from density functional theoretical (DFT) calculations based on the Becke 3-parameter hybrid exchange [20] and Lee–Yang–Parr [21] correlation density functional (B3LYP) and the Pople's split valence 6-31G(d) basis set [22]. The obtained optimum geometries were further characterized as true minima through construction and diagonalization of the Hessian matrices, this procedure providing also the harmonic vibrational frequencies that allow reliable values of the thermal corrections to the electronic energy and of the gas phase heat capacities at different temperatures to be obtained. In order to obtain more accurate energies, we have also conducted computational single-point calculations using the B3LYP correlation density functional and the extended basis-sets 6-311+G(2d,p) and 6-311+G(2df,p) [23] as well as calculations using the composite methods G3(MP2) [24] and G3(MP2)//B3LYP [25]. Method G3(MP2) is a variation of G3 [26] theory in which the basis set extensions are obtained at the second-order Møller–Plesset level, providing effectively results at the QCISD(T)/G3MP2 large level, G3MP2large being the same modification of the 6-311+G(3df,2p) as adopted in G3 theory except for the fact that the core polarization functions are not included, while G3(MP2)//B3LYP is an adaption of the previous G3(MP2) in which the geometries and zero point vibrational energies are both obtained at the B3LYP/6-31G\* level. The energies obtained at  $T = 0$  K are corrected to enthalpies at  $T = 298.15$  K by adding the vibrational, translational, rotational and the  $RT$  terms.

All calculations were performed with the Gaussian 03 series of programs [27]. NBO analysis of the wave functions has been made by using the NBO5.0 module [28] coupled to the Gaussian 03 code.

### 4. Results

#### 4.1. Experimental results

Results for the combustion experiments of 6,7-dihydro-4(5H)-benzofuranone are given in table 1. The  $\Delta_c u^0$  values are referred to the combustion reaction:

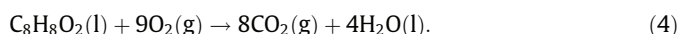


TABLE 2

DFT electronic energies<sup>a</sup>, absolute enthalpies<sup>a</sup> and thermal corrections to  $T = 298.15$  K.

Compound	$E_{\text{B3LYP/6-31G(d)}}$	$E_{\text{B3LYP/6-311+G(2d,p)}}$	$E_{\text{B3LYP/6-311+G(2df,2p)}}$	$H_{\text{G3(MP2)//B3LYP}}$	$H_{\text{G3(MP2)}}$	${}^b\text{TCE}_{\text{B3LYP/6-31G(d)}}$
H( <sup>2</sup> S)				−0.499780	−0.499478	
C( <sup>3</sup> P)				−37.788425	−37.786978	
O( <sup>3</sup> P)				−74.989704	−74.987414	
6,7-Dihydro-4(5H)-benzofuranone	−460.101587	−460.240941	−460.257219	−459.407660	−459.387693	0.153970
6,7-Dihydro-5(4H)-benzofuranone	−460.091864	−460.232138	−460.258451	−459.400142	−459.380083	0.153498
4,5-Dihydro-6(7H)-benzofuranone	−460.091771	−460.232007	−460.248317	−459.400073	−459.380026	0.153454
5,6-Dihydro-7(4H)-benzofuranone	−460.098775	−460.237838	−460.254069	−459.403595	−459.383670	0.154008
Water	−76.408953	−76.459526	−76.462564	−76.341865	−76.338625	0.024946
Methane	−40.518389	−40.534896	−40.536948	−40.420556	−40.418284	0.049030
Ethane	−79.830418	−79.858377	−79.861748	−79.651021	−79.646717	0.070651
Propane	−119.144248	−119.183774	−119.188526	−118.885804	−118.879484	0.109589
Ethene	−78.587458	−78.617640	−78.621098	−78.434968	−78.430764	0.055214
Methanal	−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
2,3-Dihydrofuran	−231.221783	−231.296883	−231.305692	−230.855782	−230.845347	0.098757
Cyclohexane	−235.880414	−235.949865	−235.958166	−235.407845	−235.395710	0.177850
Cyclohexene	−234.648295	−234.718831	−234.727343	−234.198169	−234.186286	0.153421
Cyclohexanone	−309.891254	−309.988213	−309.998405	−309.367633	−309.367618	0.159122
Cyclohexenone	−308.666132	−308.762707	−308.773080	−308.162446	−308.148275	0.098044
Furane	−230.020577	−230.093732	−230.103451	−229.674814	−229.664652	0.074862
Furfural	−343.348030	−343.457190	−343.469965	−342.867497	−342.853165	0.086270
Furan-3-carboxaldehyde	−343.345226	−343.455060	−343.467858	−342.866516	−342.851984	0.086351
Furfuryl alcohol	−344.545470	−344.665027	−344.678282	−344.057146	−344.042121	0.110515

<sup>a</sup> All energies are in a.u. ( $1 E_{\text{H}} = 2625.50184 \text{ kJ} \cdot \text{mol}^{-1}$ ).

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

The mean value and its standard deviation are given at the end of the table 1. This value was used to derive the standard molar energy and enthalpy of combustion,  $-\Delta_c U_{\text{m}}^0(\text{l}) = -(3993.5 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_c H_{\text{m}}^0(\text{l}) = -3996.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ , and the standard molar enthalpy of formation,  $\Delta_f H_{\text{m}}^0(\text{l}) = -295.4 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  of 6,7-dihydro-4(5H)-benzofuranone. In accordance with customary thermochemical practice [29], the uncertainty assigned to the standard molar enthalpy of combustion, is twice the overall standard deviation of the mean and includes the uncertainty in calibration. In order to derive  $\Delta_f H_{\text{m}}^0(\text{l})$  from  $\Delta_c H_{\text{m}}^0$ , the standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$ , at  $T = 298.15$  K,  $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$  [30] and  $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  [30], respectively, were used.

The standard molar enthalpy of vaporization of 6,7-dihydro-4(5H)-benzofuranone,  $\Delta_{\text{f}}^{\text{g}} H_{\text{m}}^0(298.15 \text{ K}) = (69.4 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$ , was determined from six independent experiments (the uncertainty is twice the standard deviation of the mean). The standard molar enthalpy of formation of 7-dihydro-4(5H)-benzofuranone, in the gaseous state, at  $T = 298.15$  K,  $\Delta_f H_{\text{m}}^0(\text{g}) = -226.0 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$ , was so obtained combining the values for standard molar enthalpy of formation in the liquid state and the standard molar enthalpy of vaporization.

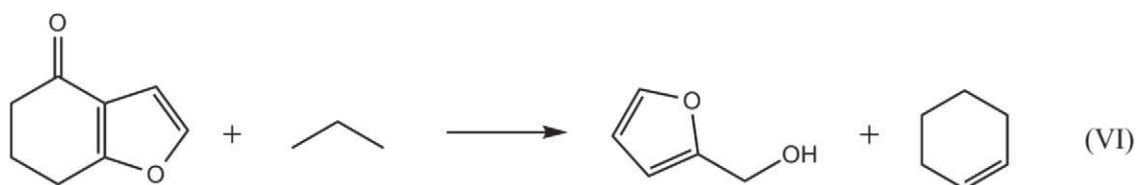
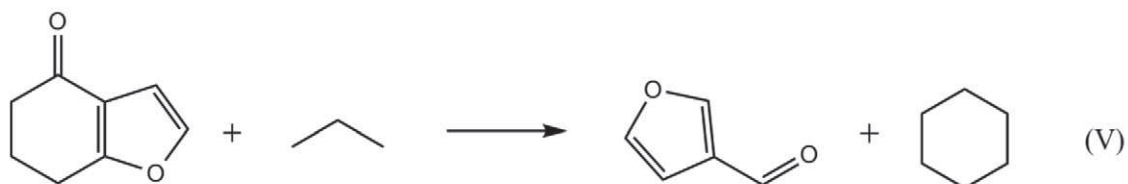
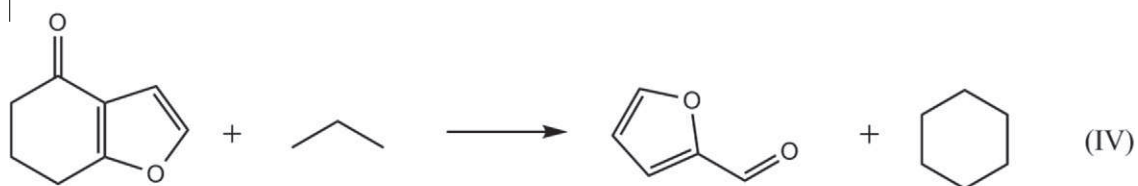
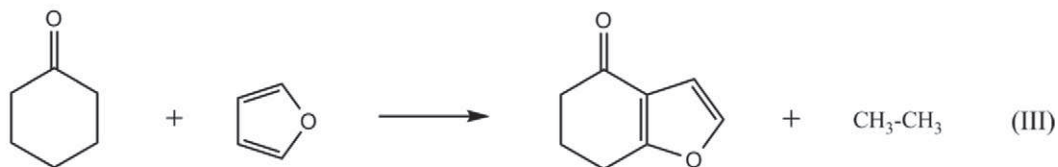
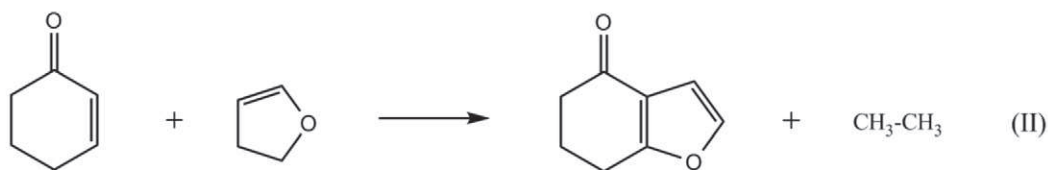
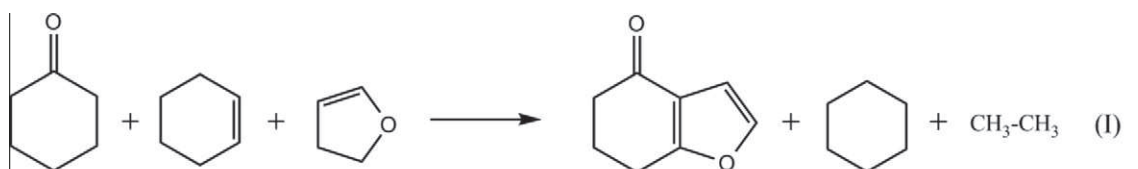
#### 4.2. Computational results and discussion

The optimum geometries of all isomeric dihydrobenzofuranones are found to correspond to almost planar conformations, since only one of the  $-\text{CH}_2-$  fragments in the six-membered ring of each molecule deviates from planarity, as a consequence of steric hindrance. In particular, the five membered (furan) ring adopts a perfectly planar conformation and the  $-\text{C}=\text{O}$  fragment is co-planar with this ring for the species 6,7-dihydro-4(5H)-benzofuranone and 5,6-dihydrobenzofuran-7(4H)-one, while for the remaining isomers the oxygen atom of this fragment deviates slightly from planarity. This behavior should have energetic consequences since planarity allows stabilizing interactions involving the  $\pi$ -lone electronic pairs of the oxygen atoms and the  $\pi$ -double bonds of both rings. Indeed, for the most stable isomer, the planar  $\text{O}-\text{C}=\text{C}=\text{O}$  moiety behaves really like an ester fragment with and intercalated  $\text{C}=\text{C}$  double bond. We have already probed the stabilizing effect of

the ester fragment for dihydrocoumarine and isochromanone [5] and even when intercalated by a C=C double bond, as in the case of chromone [31]. The isomer with this fragment is indeed found to be the most stable one. 6,7-dihydrobenzofuran-5(4H)-one and 4,5-dihydrobenzofuran-6(7H)-one are the least stable isomers due to the presence of chains of atoms containing only single bonds between both fragments which prevents the stabilizing interactions to occur. Finally, for 5,6-dihydrobenzofuran-7(4H)-one such interactions can occur even though being attenuated. These effects can be quantitatively considered and evaluated within the framework of Natural Bond Orbital (NBO) theory [32–34], according to which, the electronic population of a molecular system should be distributed over a set of localized one-centre (“lone-pair”) and two-centre (“bond”) orbitals, leading to a localized description which closely mimics a classical Lewis-type picture of the electronic system. In this context delocalization effects are evidenced by small occupancies of the set of anti-bonding orbitals, the stabilizing effect of such delocalization interactions

being quantitatively obtained as second-order perturbation estimates of the corresponding bonding–anti-bonding interactions. By doing so, we were able to identify the leading donor–acceptor interactions which are responsible for the different stabilities of the dihydrobenzofuranone isomers as being those involving the  $\pi$ -lone electronic pairs of the carbonyl oxygen atom and the anti-bonding  $\pi_{C=C}^*$  natural bonding orbital, which contributes with a stabilization energy of about  $138.1 \text{ kJ} \cdot \text{mol}^{-1}$  ( $33 \text{ kcal} \cdot \text{mol}^{-1}$ ) for both isomers where it is allowed to occur.

Choosing adequate chemical schemes which allow reliable estimates of the enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone revealed difficult due to the lack of the corresponding high quality experimental measurements for the auxiliary molecules involved. Indeed, besides the Bond Separation Reaction (BSR) involving the simplest two-heavy-atom molecules containing the same formal bonds which occur in the molecule, we only could find, in the thermochemical literature, experimental data allowing us to use the following set of isodesmic reactions:



**TABLE 3**Computational estimates of the standard enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone in the gas phase at  $T = 298.15$  K.

Compound	R	$-\Delta_f H_m^0/\text{kJ} \cdot \text{mol}^{-1}$				
		DFT/B3LYP			G3(MP2)//B3LYP	G3(MP2)
		6-31G(d)	6-311+G(2d,p)	6-311+G(2df,2p)		
6,7-Dihydro-4(5 <i>H</i> )-benzofuranone	I	253.6	238.3	239.4	214.1	215.0
	II	153.1	141.6	142.2	216.6	217.4
	III	254.6	247.3	246.6	219.7	220.5
	IV	216.6	217.4	217.3	217.1	217.6
	V	226.5	225.4	225.3	222.0	223.0
	VI	249.7	220.3	218.3	212.2	213.8
	BSR	175.3	157.3	163.4	213.9	218.2
	Atomization				222.6	219.0

Table 2 reports the total energies and absolute enthalpies, identified by the subscripts  $E_{\text{B3LYP/6-31G(d)}}$ ,  $E_{\text{B3LYP/6-311+G(2d,p)}}$ ,  $E_{\text{B3LYP/6-311+G(2df,2p)}}$ ,  $H_{\text{G3(MP2)//B3LYP}}$ ,  $H_{\text{G3(MP2)}}$  as well as the thermal corrections, TCE6-31G(d) for the studied compound and for all the auxiliary molecules used in the isodesmic reactions (I)–(VI). The values of the standard enthalpies of formation of cyclohexenone has been taken from [35] that of furan-3-carboxaldehyde from [36] and those of the remaining auxiliary molecules were obtained from Pedley's compilation [37].

Reactions II, III, IV, V, VI and BSR reveal to be those whose energetics is more accurately described by our calculations, particularly at the level of calculation involving optimized MP2/6-31G\* geometries, i.e., G3(MP2). Indeed, using those reactions, we were able to estimate the enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone with deviations from the experimental value which are not larger than about  $8.0 \text{ kJ} \cdot \text{mol}^{-1}$ . On the other hand, the estimates based on the energies obtained from DFT calculations, even when using the larger basis sets, 6-311+G(2d,p) and 6-311+G(2df,2p), are affected by much larger deviations from the experimental value, as can be seen from the results in table 3. Subsequently, we have just used the G3(MP2) and G3(MP2)//

B3LYP results to obtain estimates of the standard enthalpies of formation of the remaining isomers. Somewhat surprising is the very good accuracy of the estimate obtained with atomization reactions together with the absolute enthalpies from the G3(MP2) and G3(MP2)//B3LYP calculations. Indeed, since atomization reactions involve breaking all bonds in the molecule they are not expected to provide the cancellation of the errors in the correlation energy which is supposed to occur for isodesmic or homodesmotic reactions. Thus we were only confident to consider such estimates if they are obtained from the absolute enthalpies obtained at the G3(MP2) and G3(MP2)//B3LYP levels of calculation, which are likely include most of the correlation energy. Indeed, for those reactions we obtained estimates of the standard enthalpy of formation of 6,7-dihydro-4(5H)-benzofuranone which are in very good agreement with our experimental data. The G3(MP2)//B3LYP estimate is really within the criteria of “chemical accuracy” ( $4.19 \text{ kJ} \cdot \text{mol}^{-1}$ ) when compared with experimental data. Such good agreement do indeed lead us to suppose the estimates of the standard enthalpies of formation for the remaining isomers, reported in table 4, to be also very reliable.

### Acknowledgements

Thanks are due to Fundação para a Ciência e a Tecnologia, F.C.T., Lisbon, Portugal, and to FEDER for financial support to Centro de Investigação em Química of the University of Porto (CIQ-UP). Clara C.S. Sousa thanks the F.C.T. for the award of her doctoral scholarship (BPD/48273/2008).

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**Table 4**Computational estimates of the standard enthalpy of formation in the gas phase 6,7-dihydro-4(5H)-benzofuranone and its isomers at  $T = 298.15$  K.

Compound	$-\Delta_f H_m^0 / \text{kJ} \cdot \text{mol}^{-1}$		
	R	G3(MP2)//B3LYP	G3(MP2)
6,7-Dihydro-5(4H)-benzofuranone	I	194.4	195.0
	II	196.8	197.5
	III	200.0	200.5
	IV	197.3	197.6
	V	202.2	203.0
	VI	192.4	193.8
	BSR	194.2	198.2
	Atomization	202.9	199.0
4,5-Dihydro-6(7H)-benzofuranone	I	194.2	194.8
	II	196.7	197.4
	III	199.8	200.4
	IV	197.2	197.5
	V	202.0	202.8
	VI	192.2	193.7
	BSR	194.0	198.0
	Atomization	202.7	198.9
5,6-Dihydro-7(4H)-benzofuranone	I	203.5	204.4
	II	205.9	206.9
	III	209.0	209.9
	IV	206.4	207.0
	V	211.3	212.4
	VI	201.5	203.2
	BSR	203.3	207.6
	Atomization	212.0	208.4

BSR – Bond Separation Reaction.



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