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Experimental and computational thermochemistry of 1,4-benzodioxan and its 2-R derivatives

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ABSTRACT

The standard molar energies of combustion, at $T = 298.15$ K, of crystalline 1,4-benzodioxan-2-carboxylic acid and 1,4-benzodioxan-2-hydroxymethyl were measured by static bomb calorimetry in an oxygen atmosphere. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were obtained by Calvet microcalorimetry. These values were used to derive the standard molar enthalpies of formation of the compounds in the gas phase at $T = 298.15$ K: 1,4-benzodioxan-2-carboxylic acid $-(547.7 \pm 3.0)$ kJ · mol^{-1} and 1,4-benzodioxan-2-hydroxymethyl $-(374.2 \pm 2.3)$ kJ · mol^{-1}.

In addition, density functional theory calculations using the B3LYP hybrid exchange–correlation energy functional with extended basis sets, 6-311G** and cc-pVTZ, have been performed for the compounds studied. We have also tested two more accurate computational procedures involving multiple levels of electron structure theory in order to get reliable estimates of the thermochemical parameters of the compounds studied. The agreement between experiment and theory gives confidence to estimate the enthalpies of formation of other 2-R derivatives of 1,4-benzodioxan (R = –CH$_2$COOH, –OH, –COCH$_3$, –CHO, –CH$_3$, –CN, and –NO$_2$).

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1. Introduction

Benzene-fused ring compounds, like benzodioxan, attract particular interest since they are the major building blocks of nature. Their conformational behaviour and energetics are very important to determine the biological activity of a system [1]. It is known that chemical structures incorporating a 1,4-benzodioxan-2-yl moiety as the main feature have many interesting pharmacological properties like being one of the oldest and best-known classes of α-adrenoreceptor antagonists and they are also effective ligands of 5-HT$_{1A}$ serotoninergic receptors [2]. It is our aim with this paper to provide some experimental and computational thermodynamic parameters which can contribute to a better understanding of these systems.

In this work, we report the standard molar enthalpies of formation of 1,4-benzodioxan-2-carboxylic acid and 1,4-benzodioxan-2-hydroxymethyl in the gaseous phase, obtained from measurements of the combustion energies using a static bomb calorimeter and from the enthalpies of sublimation of the compounds measured by Calvet microcalorimetry. Experimental determinations for other 2-R derivatives of 1,4-benzodioxan were

precluded due to the impossibility to obtain pure samples of the compounds in the quantity needed. So, we have decided to perform theoretical calculations as a complement to the experimental work. Density functional theory (DFT) and multilevel calculations were conducted in order to obtain the optimized geometries of 1,4-benzodioxan-2-R with R = –COOH, –CH$_2$OH, –CH$_2$COOH, –OH, –COCH$_3$, –CHO, –CH$_3$, –CN and –NO$_2$. Estimates of the enthalpies of formation for all the derivatives were thus obtained from the DFT and multilevel calculations with appropriate isodesmic reactions.

2. Experimental section

2.1. Materials and purity control

The 1,4-benzodioxan-2-carboxylic acid [CAS 3663-80-7] and 1,4-benzodioxan-2-hydroxymethyl [CAS 3663-82-9] were obtained from Aldrich Chemical Co. The compounds were purified by repeated sublimation under reduced pressure before experimental studies. The average ratios of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample used were: 1,4-benzodioxan-2-carboxylic acid (1.0006 ± 0.0002) and 1,4-benzodioxan-2-hydroxymethyl (1.0000 ± 0.0003). The densities of the samples were estimated as 1,4-benzodioxan-2-carboxylic acid (1.10 g · cm^{-3}), 1,4-benzodioxan-2-hydroxymethyl (1.04 g · cm^{-3}).

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The purity of 1,4-benzodioxan-2-hydroxymethyl (mass fraction purity 0.9988) was also assessed by differential scanning calorimetry (DSC) using the fractional fusion technique [3]. The DSC experiments were performed on a Setaram DSC 141 calorimeter using a heating rate of $1.67 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high purity reference materials (naphthalene, benzoic acid, and indium) and its power scale was calibrated with high purity indium (mass fraction >0.99999) [4]. The samples were hermetically sealed in stainless steel crucibles. It was impossible to make a complete study of 1,4-benzodioxan-2-carboxylic acid because it decomposes during fusion, above $T = 399$ K. Nevertheless, the recorded thermograms for both compounds did not show any phase transitions between $T = 298$ K and the melting temperature of the compounds.

2.2. Combustion calorimetry

The enthalpies of combustion were measured with a static bomb calorimeter apparatus (twin valve bomb, type 1108, Parr Instrument Company). Since the apparatus and the technique have been described [5,6], only a brief description will be given here. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190p) having a massic energy of combustion, under certificated conditions, of $-\Delta_c u = (26435.1 \pm 3.5) \text{ J} \cdot \text{g}^{-1}$. Calibration experiments as well as the combustion experiments for the compounds were carried out in oxygen at a pressure of 3.04 MPa. The 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 seven independent calibration experiments performed $\varepsilon_{cal} = (16004.8 \pm 1.6) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

For all the experiments, the compounds were burnt in pellet form with 1.00 cm^3 of water added to the bomb. Samples were ignited at $T = 298.15$ K. The electrical energy for ignition, $\Delta U(\text{ign.})$, was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire,

$$\Delta U(\text{IBP}) = -\{\varepsilon_{cal} + \Delta m(H_2O) \cdot c_p(H_2O, l) + \varepsilon_f\}\Delta T_{ad} + \Delta U_{ign}, \quad (1)$$

where $\Delta U(\text{IBP})$ is the energy associated with the isothermal bomb process, ε_f is the energy of the bomb contents after ignition, and ΔT_{ad} is the adiabatic temperature rise calculated using the program LABTERMO [7]. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, the value of $-16250 \text{ J} \cdot \text{g}^{-1}$ [8] was taken for the massic energy of combustion, $\Delta_c u^o$ (the value has been confirmed in our laboratory). The energetic correction for nitric acid formation $\Delta U(HNO_3)$ was based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [9] for the molar energy of formation of 0.1 $\text{mol} \cdot \text{dm}^{-3}$ $HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. The mass of compound, $m(\text{compound})$, used in each experiment was determined from the total mass of carbon dioxide, $m(CO_2, \text{total})$, produced after allowance for that formed from the cotton-thread fuse.

An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ at $T = 298.15$ K, a typical value for most organic compounds, was assumed [10]. For each compound, the corrections to the standard state, ΔU_Σ, to derive the standard massic energy of combustion, $\Delta_c u^\circ$, were made by the procedure given by Hubbard *et al.* [11]. The atomic weights of the elements were those recommended by the IUPAC commission [12].

2.3. Calvet microcalorimetry

The standard molar enthalpies of sublimation were measured using the "vacuum sublimation" drop microcalorimetric method

[13]. Samples, about (3 to 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 $T = 390$ K for 1,4-benzodioxan-2-carboxylic acid and at $T = 375$ K for 1,4-benzodioxan-2-hydroxymethyl. Then the samples were 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. The observed enthalpies of sublimation were then corrected to $T = 298.15$ K using the equation,

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

where T is the temperature of the hot reaction vessel, $C_{p,m}^\circ$ (g) represents the molar heat capacity of the compound 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* basis set:

1,4-Benzodioxan-2-carboxylic acid:

$$C_{p,m}^\circ (g)/(J \cdot mol^{-1} \cdot K^{-1}) = -0.000448(T/K)^2 + 0.842(T/K) - 37.606, \quad (3)$$

1,4-Benzodioxan-2-hydroxymethyl:

$$C_{p,m}^\circ (g)/(J \cdot mol^{-1} \cdot K^{-1}) = -0.000383(T/K)^2 + 0.806(T/K) - 35.488. \quad (4)$$

The microcalorimeter was calibrated *in situ* for these measurements using the reported enthalpy of sublimation of naphthalene [14].

3. Computational details

The geometries of all compounds were optimized using the density functional theory (DFT) with the Becke 3-parameter hybrid exchange [15] and Lee–Yang–Parr [16] correlation density functional (B3LYP) and two different basis sets: the 6-31G* [17] and the 6-311G** [18]. The resulting optimum geometries were further characterized as true minima through construction and diagonalization of the B3LYP/6-31G* Hessian matrices. This procedure provided the harmonic vibrational frequencies and thermal corrections, which are needed to estimate enthalpies at the temperature of 298.15 K. More accurate energies were further obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using DFT theory and the triple-zeta correlation consistent basis set cc-pVTZ [19] and also using two much more accurate correlated computational techniques of the MCCM/3 suite [20,21] described later. Unless otherwise stated, all calculations were performed using the UK version of GAMESS [22,23]. The MCCM/3 calculations have been performed using the MLGAUSS program version 2.0 [24], which relies on the Gaussian 03 series of programs [25]. The NBO analysis of the wavefunctions has been performed with the NBO 5 program [26] incorporated in the Gaussian 03 series of programs [25].

4. Experimental results

The temperature and enthalpy of fusion of 1,4-benzodioxan-2-hydroxy methyl were measured using a differential scanning calorimeter and are, respectively, $T_{fus} = (362.40 \pm 0.12)$ K, $\Delta_{cr}^l H_m^\circ(T_{fus}) = (28.78 \pm 0.10) \text{ kJ} \cdot \text{mol}^{-1}$. The values for T_{fus} were observed at the onset of the calorimetric peak. The 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 each compound are given in table 1. The individual results of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in table 2. The derived standard molar energies, $\Delta_c U_m^\circ$ (cr), and enthalpies of combustion, $\Delta_c H_m^\circ$ (cr), and the standard molar enthalpies of formation, $\Delta_f H_m^\circ$(cr), of the studied compounds are in table 3.

In accordance with customary thermochemical practice [27], 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 $\Delta_f H_m^\circ$ (cr)

TABLE 1
Typical combustion experiments, at $T = 298.15$ K

	1,4-Benzodioxan-2-carboxylic acid	1,4-Benzodioxan-2-hydroxymethyl
$m(CO_2$, total)/g	1.45670	1.44774
m(cpd)/g	0.66071	0.60554
m'(fuse)/g	0.00253	0.00272
ΔT_{ad}/K	0.9237	1.0244
ε_f/(J · K^{-1})	15.65	16.04
Δm(H$_2$O)/g	0.1	0.0
$-\Delta U$(IBP)/J	14797.53	16411.00
ΔU(fuse)/J	0.53	8.90
ΔU(HNO$_3$)/J	41.09	44.17
ΔU(ign.)/J	0.95	0.75
$\Delta U\Sigma$/J	11.69	10.33
$-\Delta_c u^\circ$/(J · g^{-1})	22315.72	26996.73

TABLE 2
Individual values of the massic energy of combustion, at $T = 298.15$ K

1,4-Benzodioxan-2-carboxylic acid, $-\langle\Delta_c u^{circ}\rangle$/(J · g^{-1})	1,4-Benzodioxan-2-hydroxymethyl, $-\langle\Delta_c u^0\rangle$/(J · g^{-1})
22326.19	27000.08
22304.24	27017.55
22323.28	26996.73
22291.99	27003.18
22321.02	26998.98
22300.98	26979.76
22315.72	27003.56
22298.63	27018.18
	$-\langle\Delta_c u^{circ}\rangle$/(J · g^{-1})
22310.3 ± 4.6	27002.3 ± 4.3

TABLE 3
Derived standard ($p^\circ = 0.1$ MPa) molar values, at $T = 298.15$ K

Compound	$-\Delta_c U_m^\circ$/ (kJ · mol^{-1})	$-\Delta_c H_m^\circ$/ (kJ · mol^{-1})	$-\Delta_f H_m^\circ$(cr)/ (kJ · mol^{-1})
1,4-Benzodioxan-2-carboxylic acid	4019.4 ± 1.9	4019.4 ± 1.9	665.5 ± 2.2
1,4-Benzodioxan-2-hydroxymethyl	4487.1 ± 1.8	4489.6 ± 1.8	481.1 ± 2.2

TABLE 4
Derived standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation at $T = 298.15$ K

Compound	$-\Delta_f H_m^\circ$ (cr)/ (kJ · mol^{-1})	$\Delta_{cr}^g H_m^\circ$/ (kJ · mol^{-1})	$-\Delta_f H_m^\circ$ (g)/ (kJ · mol^{-1})
1,4-Benzodioxan-2-carboxylic acid	665.5 ± 2.2	117.8 ± 2.1	547.7 ± 3.0
1,4-Benzodioxan-2-hydroxymethyl	481.1 ± 2.2	106.9 ± 0.8	374.2 ± 2.3

from $\Delta_c H_m^\circ$ (cr), the standard molar enthalpies of formation of H$_2$O(l) and CO$_2$(g), at $T = 298.15$ K, $-(285.830 ± 0.042)$ kJ · mol^{-1} [28] and $-(393.51 ± 0.13)$ kJ · mol^{-1} [28], respectively, were used.

The standard molar enthalpies of sublimation, $\Delta_{cr}^g H_m^\circ$(298.15 K), were determined from six independent experiments for which the uncertainty is twice the standard deviation of the mean. To obtain the standard molar enthalpies of sublimation, at $T = 298.15$ K, the observed enthalpies in each experiment, at T/K, were corrected using equations (2) to (4).

Combining the values of the standard molar enthalpies of sublimation and the standard molar enthalpies of formation in the condensed phase leads to the values of the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K. The values are listed in table 4.

5. Theoretical results and discussion

The geometries of all molecules have been fully optimized as described. With the exception of –OH and –NO$_2$, all studied substituents are observed to prefer the equatorial position when attached to the position 2 of the dioxane ring, a preference which agrees, for instance, with similar behaviour of substituted cyclohexanes. This relative preference of the equatorial position over the axial one is usually explained as a consequence of the ability to avoid the axial–axial interactions. In the case of the –OH and NO$_2$ substituents, the preference for the axial position can be attributed to the enhancement of hyper-conjugative interactions involving the π-lone electronic pair of the ring oxygen atom closest to the substituent and the sigma anti-bonding orbital involving the substituent oxygen or nitrogen atom and the carbon ring atom directly attached to it. This hyper-conjugative interaction is responsible for the so-called anomeric effect which is well known to occur within –O–C–O– fragments. In fact, additional NBO analysis of the B3LYP/6-311G** wavefunction for the OH substituted benzodioxan reveals that the donor–acceptor interactions involving the lone-electronic pair of the axial substituent oxygen atom and the anti-bonding σ_{O6-C7}^* NBO (see figure 1 for atom numbering). contributes a stabilization energy of about 17 kJ · mol^{-1}, as estimated by simple second-order perturbation theory. The corresponding interaction involving the lone-electronic pair of atom O6 and the anti-bonding σ_{C7-O11}^* NBO contributes a stabilization energy of about 12 kJ · mol^{-1}. In the case of the equatorial substitution, a similar perturbation analysis results in homologous stabilization interactions of about (13 and 4) kJ · mol^{-1}. Also, for the NO$_2$ substituted benzodioxan, similar observations can be obtained from the NBO analysis, implying that the interaction of the lone electronic pair of the O6 atom with the anti-bonding σ_{C7-N}^* NBO contributes a stabilization energy of about 19 kJ · mol^{-1}, while the homologous interaction when the substituent is in the equatorial position only amounts to about 6 kJ · mol^{-1}. Thus, the NBO analysis of the interaction energies clearly supports the hyper-conjugative interactions as an important factor determining the preference for the axial substitution.

In order to estimate the enthalpies of formation of the systems from the calculated energies, we used the following reaction
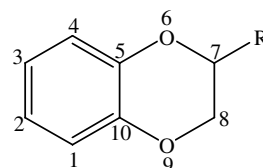

FIGURE 1. Atom numbering scheme for the geometric results of the 1,4-benzodioxan derivatives.

involving auxiliary systems whose thermochemical properties are well established experimentally [29]. For 1,4-benzodioxan, we have used the experimental value $-(178.3 \pm 2.5)\,kJ \cdot mol^{-1}$ [30].

tion methods (MCCM's), have the enormous advantage of scaling as N^6 or even as N^5, while essentially maintaining a high level of accuracy. In this work, we decided to test two of the methods of

(R= $-COOH$, $-CH_2OH$, $-CH_2COOH$, $-OH$, $-COCH_3$, $-CHO$, $-CH_3$, $-CN$, $-NO_2$)

(5)
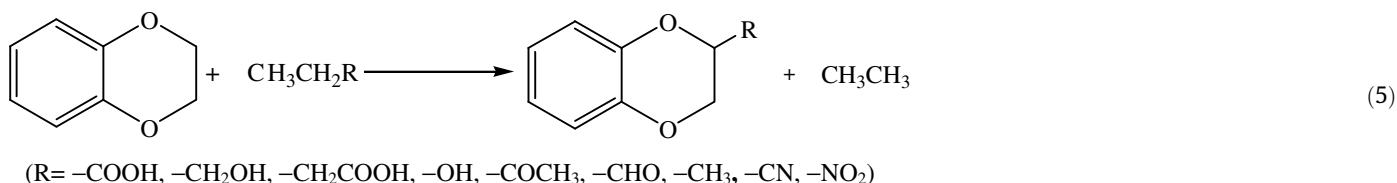
Even though the above mentioned DFT calculations of the molecular energies can provide sufficiently good results for most purposes, it is often observed that they lack the capacity of describing reaction energetics with the accuracy required in thermochemistry, unless specific reaction types are used, *i.e.*, isodesmic or homodesmic. To obtain such accurate results, we must go further in the treatment of electronic correlation. The usual ways of dealing with the electron correlation problem involve very costly computationally procedures, which, as such, can only be applied to a very limited set of moderately sized systems. However, accurate methods involving the combination of results from different levels of electronic structure theory and/or different one-electron basis sets have been proposed [31–35]. These usually involve empirical parameters and extrapolation to a more accurate result than that produced by the most accurate component calculation. The resulting accuracy amounts to $\pm 1\,kcal \cdot mol^{-1}$. These methods, referred to as multilevel methods, constitute a very powerful alternative to single-level methods. Unfortunately, the computational cost of most of the methods rises as N^7, where N is the number of atoms. Thus they are not usable for moderately sized systems. More recently, a series of multilevel methods using both correlated wave function methods and density functional methods have been proposed [20,21]. These methods, called multi-coefficient correla-

the MCCM/3 [20] suite, namely the MC-UT/3 and MCQCISD/3, which are methods scaling as N^6. In the calculations, we used the B3LYP/6-311G** geometries obtained earlier and all the MC-UT/3 and MCQCISD/3 calculations were performed using the MLGAUSS program, version 2.0 [24]. This program uses the Gaussian 03 series of programs [25].

Total energies, identified by the subscripts B3LYP/6-311G**, B3LYP/cc-pVTZ, MCUT and MCQCISD as well as thermal corrections, TCE/6-31G*, are reported in table 5 for the 1,4-benzodioxan derivatives. 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 resulting estimates of the enthalpies of formation are provided in table 6, for all the derivatives. We must note that both the B3LYP/6-311G** and the B3LYP/cc-pVTZ estimates show good agreement with the available experimental estimates, with absolute unsigned errors of $5.6\,kJ \cdot mol^{-1}$ (B3LYP/6-311G**) and $6.7\,kJ \cdot mol^{-1}$ (B3LYP/cc-pVTZ) for 1,4-benzodioxan-2-carboxylic acid, and of $3.7\,kJ \cdot mol^{-1}$ (B3LYP/6-311G**) and $7.4\,kJ \cdot mol^{-1}$ (B3LYP/cc-pVTZ) for 1,4-benzodioxan-2-hydroxymethyl. However, if we consider the more accurate energies obtained from the MCUT/3 or from the MCQCISD/3 multi-coefficient correlated calculations we obtain much better estimates. In this case absolute un-

TABLE 5
Electronic energies and thermal corrections to $T = 298.15$ K

Compound	$E_{\text{B3LYP/6-311G}^{**}}$	$E_{\text{B3LYP/cc-pVTZ}}$	E_{MCUT}	E_{MCQCISD}	$TCE_{\text{B3LYP/6-31G}^*}$ [a]
1,4-Benzodioxan	−460.218270	−460.268935	−459.499477	−459.506267	0.148055
1,4-Benzodioxan-2-yl methyl ketone	−612.902961	−612.968234	−611.962605	−611.970754	0.187048
1,4-Benzodioxan-2-hydroxymethyl	−574.776286	−574.840037	−573.913395	−573.922457	0.182234
1,4-Benzodioxan-2-carboxaldehyde	−573.564536	−573.626492	−572.691754	−572.699989	0.158270
1,4-Benzodioxan-2-carboxylic acid	−648.852965	−648.922664	−647.881232	−647.891970	0.165431
1,4-Benzodioxan-2-nitro	−664.774575	−664.846687	−663.798558	−663.809355	0.152904
1,4-Benzodioxan-2-methyl	−499.545850	−499.600270	−498.765015	−498.771873	0.176489
1,4-Benzodioxan-2-ethanoic acid	−688.175418	−688.248711	−687.147601	−687.157528	0.193708
1,4-Benzodioxan-2-cyano	−552.485741	−552.545356	−551.624332	−551.624332	0.148621
1,4-Benzodioxan-2-hydroxy	−535.466756	−535.525404	−534.663843	−534.671518	0.153467
Ethane	−79.857272	−79.865585	−79.713342	−79.714008	0.075856
Propanoic acid	−268.485206	−268.513314	−268.098100	−268.102624	0.093252
Propanol	−194.414748	−194.436549	−194.119874	−194.122905	0.110463
Butanoic acid	−307.809869	−307.841732	−307.355813	−307.360474	0.12212
Ethanol	−155.089963	−155.108113	−154.862309	−154.865239	0.081546
Butanone	−232.541404	−232.565150	−232.175000	−232.177036	0.115380
Propanal	−193.203063	−193.223457	−192.904620	−192.906744	0.086754
Propane	−119.182194	−119.194292	−118.971133	−118.971901	0.104692
Cyanoethane	−172.119767	−172.137344	−171.838856	−171.839583	0.076677
Nitroethane	−284.414400	−284.445113	−284.011910	−284.016727	0.081552

[a] All energies are in a.u. (1 E_H = 2625.50184 kJ · mol^{-1}).
[b] $TCE_{\text{B3LYP/6-31G}^*} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{zp}} + \Delta_{0\,K}^{298.15\,K} E_{\text{vib}}$.

TABLE 6

Theoretical estimates of the standard enthalpies of formation in the gas phase at $T = 298.15$ K of 1,4-benzodioxan-2-R

Compound	$\Delta_f H_m^\circ(g)/(kJ \cdot mol^{-1})$			
	6-311G**	cc-pVTZ	MC-UT/3	MC-QCISD/3
1,4-Benzodioxan-2-yl methyl ketone	−335.9	−333.7	−338.3	−338.2
1,4-Benzodioxan-2-carboxaldehyde	−283.1	−281.1	−284.5	−284.5
1,4-Benzodioxan-2-nitro	−196.9	−194.4	−200.4	−200.0
1,4-Benzodioxan-2-carboxylic acid	−542.1	−541.0	−544.1	−544.3
1,4-Benzodioxan-2-hydroxymethyl	−370.5	−366.8	−370.9	−370.7
1,4-Benzodioxan-2-hydroxy	−371.9	−367.0	−370.9	−367.2
1,4-Benzodioxan-2-ethanoic acid	−565.9	−563.5	−568.8	−566.6
1,4-Benzodioxan-2-methyl	−217.8	−217.1	−220.9	−220.9
1,4-Benzodioxan-2-cyano	−0.9	−0.2	−3.1	−3.1

signed errors of 3.6 kJ · mol^{-1} (MCUT/3) and 3.4 kJ · mol^{-1} (MCQCISD) for 1,4-benzodioxan-2-carboxylic acid and of 3.3 kJ · mol^{-1} (MCUT/3) and 3.7 kJ · mol^{-1} (MCQCISD) for 1,4-benzodioxan-2-hydroxymethyl are obtained. The average value of the deviations is now only 3.5 kJ · mol^{-1} for each molecular system, a fact that reveals a remarkable amelioration of the results relative to the previous B3LYP estimates and qualifies them as being already within the limits usually accepted for the standard of "chemical accuracy", *i.e.*, deviations lower than 1 kcal · mol^{-1}. Thus, our best results provide clear evidence of the reliability of the multi-coefficient correlation methods towards obtaining very accurate computational estimates of thermochemical parameters with affordable computational cost.

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