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Energetics of Hydroxytetralones: A Calorimetric and Computational Thermochemical Study

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The standard ($p° = 0.1$ MPa) molar energies of combustion in oxygen at $T = 298.15$ K of 5-hydroxy- and 6-hydroxy-α-tetralone were measured by static bomb calorimetry. The values of the standard molar enthalpies of sublimation at $T = 298.15$ K were obtained by Calvet microcalorimetry. Combining these results, the standard molar enthalpies of formation of the compounds in the gas-phase at $T = 298.15$ K have been calculated: 5-hydroxy-α-tetralone $-(262.5 \pm 2.3)$ $\text{kJ}\cdot\text{mol}^{-1}$ and 6-hydroxy-α-tetralone $-(268.1 \pm 2.2)$ $\text{kJ}\cdot\text{mol}^{-1}$. Additionally, high-level single-point calculations based on density functional theory with the B3LYP hybrid exchange-correlation energy functional and extended basis sets as well as on two more accurate correlated computational techniques of the MCCM/3 suite have been performed for the studied compounds. The agreement between experiment and theory gives us confidence to estimate the enthalpies of formation of 7-hydroxy and 8-hydroxy-α-tetralone. Similar calculations were done for 5-, 6-, 7-, and 8-hydroxy-*β*-tetralone, for which experimental work was not done.

Introduction

α-Tetralone and *β*-tetralone derivatives, in particular, hydroxytetralones, occupy an important position in organic synthesis as target molecules of biological and pharmacological interest. 5-Hydroxy-α-tetralone is an intermediate in the synthesis of Levobunolol, which finds application as a biochemical reagent to test blood sugar and to produce an ophthalmic solution used in the lowering of intraocular pressure whether or not accompanied by glaucoma.[1] A microdetection system for glycosphingolipid analysis has been developed, which also employs 5-hydroxy-α-tetralone as the fluorescent labeling reagent.[2] 6-Hydroxy-α-tetralone is a precursor in the synthesis of estradiol,[3] and 7-hydroxy-α-tetralone is a precursor in the synthesis of structural analogues of sialyl Lewis^x, which is one of the most important blood group antigens and is displayed on the terminus of glycolipids that are present on the cell surface.[4]

Substituted *β*-tetralones also play an important role in organic synthesis as a result of their high reactivity and suitability as starting materials for a wide range of synthetic heterocyclic compounds and pharmaceuticals with biological activities.[5]

In this work, we present the experimental values of the enthalpies of formation in both condensed and gas-phase 5-hydroxy-α-tetralone and 6-hydroxy-α-tetralone. We also discuss the estimates of the enthalpies of formation in the gas-phase that are obtained from density functional theory (DFT) calculations and from more accurate correlated computational techniques of the MCCM/3 suite for other hydroxy isomers of α- and *β*-tetralones.

Experimental Section

Materials. Commercial samples of 5-hydroxy-α-tetralone [28315-93-7] and 6-hydroxy-α-tetralone [3470-50-6] were obtained from Aldrich Chemical Co. at a stated mass fraction of 0.99 and 0.999, respectively.

The compounds were purified by sublimation under reduced pressure, and their purity was assessed using differential scanning calorimetry (DSC) by a fractional fusion technique.[6] The samples, hermetically sealed in stainless steel crucibles, were heated at $(1.67\cdot10^{-2})\text{K}\cdot\text{s}^{-1}$. The temperature scale of the calorimeter was calibrated by measuring the melting temperature of three high-purity reference materials (naphthalene, benzoic acid, and indium),[7] and its power scale was calibrated with high-purity indium (mass fraction > 0.99999).

The purity of the samples was also confirmed through the carbon dioxide recovery ratios. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were 5-hydroxy-α-tetralone (100.00 ± 0.01) and 6-hydroxy-α-tetralone (99.98 ± 0.02). The densities of the samples were estimated from the mass and the dimensions of pellets of the crystalline compounds to be 5-hydroxy-α-tetralone (1.00) $\text{g}\cdot\text{cm}^{-3}$ and 6-hydroxy-α-tetralone (0.99) $\text{g}\cdot\text{cm}^{-3}$.

Combustion Calorimetry. The standard molar enthalpies of combustion of the compounds in the condensed phase were obtained from combustion calorimetry with a static bomb calorimeter. The apparatus and technique have been previously described.[8,9] Benzoic acid (NBS thermochemical standard 39j) was used for calibration of the bomb. Its massic energy of combustion is $-\Delta_c u = (26\,434 \pm 3)\ \text{J}\cdot\text{g}^{-1}$ under certificate conditions. 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 $\varepsilon_{\text{cal}} = (16\,012.8$

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Table 1. Temperatures of Fusion, T_{fus}, and Solid/Solid Phase Transition, T_{trans}, Enthalpies of Fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{0}(T_{\mathrm{fus}})$, and of Solid/Solid Phase Transition, $\Delta_{\mathrm{trans}}H_{\mathrm{m}}^{0}(T_{\mathrm{trans}})$, and Purity (%) of the Studied Hydroxytetralones

compd	T_{fus} / K	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{0}(T_{\mathrm{fus}})$ / kJ·mol^{-1}	T_{trans} / K	$\Delta_{\mathrm{trans}}H_{\mathrm{m}}^{0}(T_{\mathrm{trans}})$ / kJ·mol^{-1}	purity (%)
5-hydroxy-α-tetralone	480.06 ± 0.05	33.67 ± 0.25			99.81
6-hydroxy-α-tetralone	425.91 ± 0.14	18.98 ± 0.29	387.46 ± 0.27	13.02 ± 1.23	98.94

± 1.1) 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; ΔU_{Σ} is the correction to the standard state. The remaining quantities are as previously described.[10] For the cotton thread fuse, empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, $\Delta_c u° = -16\,250$ J·g^{-1}.[11] This value has been confirmed in our laboratory. The corrections for nitric acid formation $\Delta U(\mathrm{HNO_3})$ were based on -59.7 kJ·mol^{-1}[12] for the molar energy of formation of 0.1 mol·dm^{-3} $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2}$, $\mathrm{O_2}$, and $\mathrm{H_2O(l)}$. The mass of compound, m(compound), used in each experiment was determined from the total mass of carbon dioxide, $m(\mathrm{CO_2}$, 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.[10] As samples were ignited at $T = 298.15$ K

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

where ΔU(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 increase calculated using the program LABTERMO.[13] For each compound, the corrections to the standard state, ΔU_{Σ}, to derive the standard massic energy of combustion, $\Delta_c u°$, were made by the procedure given by Hubbard et al.[14] The atomic weights of the elements were those recommended by the IUPAC commission in 2005.[15]

Calvet Microcalorimetry. The standard molar enthalpies of sublimation of the compounds were measured using the "vacuum sublimation" drop microcalorimetric method.[16] Samples of about (3 to 5) mg in thin glass capillary tubes sealed at one end were dropped at room temperature in the hot vessel in a high-temperature Calvet microcalorimeter held at convenient temperature ($T = 469$ K for 5-hydroxy-α-tetralone and $T = 448$ K for 6-hydroxy-α-tetralone) and then removed from the hot zone by vacuum sublimation. We determined the thermal corrections for the glass capillary tubes in separate experiments and minimized them, as far as possible, by dropping tubes of nearly equal mass in 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 sublimation of naphthalene.[17]

From six independent experiments, we have obtained a mean value for the observed standard molar enthalpies 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, $\Delta_{298.15\mathrm{K}}^{T}H_{\mathrm{m}}^{0}(\mathrm{g})$, using the equation

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

where T is the temperature of the hot reaction vessel and $C_{p,\mathrm{m}}^{0}(\mathrm{g})$ 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.

5-hydroxy-α-tetralone

$$C_{p,\mathrm{m}}^{0}(\mathrm{g})/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}}) = -0.000400(T/\mathrm{K})^2 + 0.817(T/\mathrm{K}) - 38.725 \quad (3)$$

6-hydroxy-α-tetralone

$$C_{p,\mathrm{m}}^{0}(\mathrm{g})/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}}) = -0.000409(T/\mathrm{K})^2 + 0.827(T/\mathrm{K}) - 41.269 \quad (4)$$

Computational Details

The geometries of all molecules have been fully optimized using DFT with the Becke three-parameter hybrid exchange[18] and the Lee–Yang–Parr[19] correlation density functionals (B3LYP) and the Pople's split-valence 6-31G* extended basis set.[20] We further certified the optimum structures so obtained as true minima by constructing and diagonalizing the corresponding Cartesian Hessian matrix; this procedure also provided 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] These final optimized structures were then used to perform single-point DFT calculations with the cc-pVTZ basis set[23] as well as energy calculations based on more accurate correlated computational techniques of the MCCM/3 suite,[24,25] viz. MCUT and MCQCISD. The latter calculations were conducted as a means of accounting, at least in part, for the correlation energy, while still maintaining the computational cost within comportable levels. We have thus selected two of the methods proposed in the MCCM/3 suite; one of them (MCUT) is based on perturbational theoretical techniques, whereas the other (MCQCISD) is based on configuration interaction methodologies.

All of the geometry optimizations, vibrational analysis, and single-point calculations have been performed using the UK version of program GAMESS.[26,27] The MCCM/3 series of calculations has been performed using the MLGAUSS driver program version 2.0,[28] which relies on the Gaussian 03 series of programs.[29] Natural bond orbital (NBO) analysis of the B3LYP/6-311G** wave functions have been performed using the NBO 5.0 program.[30]

Experimental Results

The temperatures of fusion, T_{fus} (observed at the onset of the calorimetric peaks), and of solid/solid phase transition T_{trans}, the enthalpies of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{0}(T_{\mathrm{fus}})$, and of solid/solid phase

Table 2. Typical Combustion Experiments at T = 298.15 K

	5-hydroxy-α-tetralone	6-hydroxy-α-tetralone
$m(CO_2, \text{total})/\text{g}$	1.63032	1.71959
$m(\text{cpd})/\text{g}$	0.59925	0.63239
$m(\text{fuse})/\text{g}$	0.00263	0.00222
$\Delta T_{ad}/\text{K}$	1.1513	1.2139
$\varepsilon_f/(\text{J}\cdot\text{K}^{-1})$	16.08	15.85
$\Delta m(H_2O)/\text{g}$	0.0	0.0
$-\Delta U(\text{IBP})/\text{J}$	18 454.05	19 456.17
$\Delta U(\text{fuse})/\text{J}$	42.71	36.05
$\Delta U(HNO_3)/\text{J}$	0.94	9.85
$\Delta U(\text{ign.})/\text{J}$	0.88	1.01
$\Delta U_\Sigma/\text{J}$	11.15	11.86
$-\Delta_c u°/(\text{J}\cdot\text{g}^{-1})$	30 702.37	30 674.76

Table 3. Individual Values of the Massic Energies of Combustion at T = 298.15 K

$-\Delta_c u^0/(\text{J}\cdot\text{g}^{-1})$	
5-hydroxy-α-tetralone	6-hydroxy-α-tetralone
30 705.79	30 670.17
30 702.81	30 680.77
30 695.53	30 664.93
30 696.65	30 677.67
30 702.37	30 674.76
30 713.81	30 665.69
	30 677.57
	30 679.50
$-\langle\Delta_c u^0\rangle/(\text{J}\cdot\text{g}^{-1})$	
30 702.8 ± 2.7	30 673.9 ± 2.2

Table 4. Derived Standard ($p°$ = 0.1 MPa) Molar Values at T = 298.15 K

compd	$-\Delta_c U^0_m$ kJ·mol^{-1}	$-\Delta_c H^0_m$ kJ·mol^{-1}	$-\Delta_f H^0_m(\text{cr})$ kJ·mol^{-1}
5-hydroxy-α-tetralone	4979.6 ± 1.2	4983.3 ± 1.2	381.0 ± 1.8
6-hydroxy-α-tetralone	4974.9 ± 1.1	4978.6 ± 1.1	385.6 ± 1.7

Table 5. Derived Standard ($p°$ = 0.1 MPa) Molar Enthalpies of Formation at T = 298.15 K

compd	$-\Delta_f H^0_m(\text{cr})$ kJ·mol^{-1}	$\Delta^g_{cr} H^0_m$ kJ·mol^{-1}	$-\Delta_f H^0_m(\text{g})$ kJ·mol^{-1}
5-hydroxy-α-tetralone	381.0 ± 1.8	118.5 ± 1.5	262.5 ± 2.3
6-hydroxy-α-tetralone	385.6 ± 1.7	117.5 ± 1.4	268.1 ± 2.2

transition, $\Delta_{\text{trans}}H^0_m(T_{\text{trans}})$, and the purity (%) of the compounds were obtained from the DSC experiments.

The recorded thermograms for 5-hydroxy-α-tetralone did not show any phase transition between 298.15 K and the melting temperature of the sample. For the 6-hydroxy-α-tetralone, we observed a phase transition at T = (387.46 ± 0.27) K, which corresponds to an enthalpy of phase transition of (13.02 ± 1.23) kJ·mol^{-1}. The values are reported in Table 1 and are referred to the mean values of six independent experiments on fresh samples, and the uncertainties are twice the standard deviation of the mean.

Table 2 lists a typical combustion experiment for each of the studied compounds, which correspond to the combustion reaction

$$C_{10}H_{10}O_2 + 23/2O_2 \rightarrow 10CO_2 + 5H_2O \qquad (5)$$

Table 3 lists the individual values for the combustion experiments of the two isomers, whereas Table 4 shows the derived standard molar energies and enthalpies of combustion, $\Delta_c U^0_m(\text{cr})$ and $\Delta_c H^0_m(\text{cr})$, and the standard molar enthalpies of formation of the two isomers in the crystalline phase, $\Delta_f H^0_m(\text{cr})$, at T = 298.15 K. In accordance with customary thermochemical practice,[31] 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. To derive $\Delta_f H^0_m(\text{cr})$ from $\Delta_c H^0_m(\text{cr})$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$ at T = 298.15 K, −(285.830 ± 0.042) kJ·mol^{-1}[32] and −(393.51 ± 0.13) kJ·mol^{-1},[32] respectively, were used.

The standard molar enthalpies of sublimation of the compounds at the temperature T = 298.15 K were obtained from six independent microcalorimetric experiments. The uncertainty of the results is twice the standard deviation of the mean.

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. These results are summarized in Table 5.

Computational Results and Discussion

At their optimum structures, the molecules studied in this work show conformational characteristics that very much resemble those found for the parent nonsubstituted tetralones[33] and the methoxytetralone isomers.[34] Indeed, we observe that, mainly as a consequence of the repulsions between proximate $-CH_2-$ groups, the nonbenzenic rings of these systems are considerably distorted from planarity. We refer the readers to a detailed analysis of the conformational behavior and of the factors determining the different amounts of ring distortion observed for the α-tetralone and the β-tetralone groups of isomers we published elsewhere.[33,34] We just observe that β-tetralones show much more distorted nonbenzenic rings, whereas the lower distortion of the nonbenzenic rings of α-tetralones still allows the extended electronic delocalization involving the C=O fragment and the aromatic ring. These conformational differences will certainly manifest themselves through differences in the relative stability of the isomers, as we will show later. Besides this conformational behavior, the case of 8-hydroxy-α-tetralone is interesting because an intramolecular hydrogen bond occurs that involves the hydroxyl group as the donor group and the carbonyl group as the acceptor. This hydrogen bond is special in that it allows the formation of another closed ring of atoms, thus enabling further circular electronic delocalization to occur. This fact can qualify this hydrogen bond as a resonance-assisted hydrogen bond (RAHB).[35,36] This particular type of hydrogen bond constitutes one of the strongest types of H-bond-type interactions[35,36] and has been identified and reported for other systems.[37] To assess the energetic effect of this interaction quantitatively, we have also optimized the alternative conformation of 8-hydroxy-α-tetralone with the O−H fragment rotated by 180° about the C−O bond, thus inhibiting the H-bond interaction. We will later consider the energetic effect of this inhibition, but for now, we will just use the obtained optimized geometrical bond parameters to help us support the qualification of the O−H···O interaction as an RAHB. In fact, we can observe that upon the hydrogen bond formation, the following changes in the relevant bond lengths occur: $O_{12}-H_{13}$ from 0.964 Å to 0.989 Å, $C_1=O_{11}$ from 1.214 Å to 1.235 Å, $C_8=C_9$ from 1.419 Å to 1.424 Å, C_1-C_9 from 1.497 Å to 1.467 Å, and C_8-O_{12} from 1.353 Å to 1.337 Å. Therefore, a notorious equalization of bond lengths occurs within the newly formed ring structure, which constitutes a clear support of the conjecture of the RAHB nature of the associated interaction. The energetic difference between the two conformers is predicted to be on the order of 60 kJ·mol^{-1}, a value that is

Table 6. Calculated Electronic Energies and Thermal Corrections to T = 298.15K

compd	$E_{\mathrm{B3LYP/6\text{-}311G^{**}}}$	$E_{\mathrm{B3LYP/cc\text{-}pVTZ}}$	E_{MCUT}	E_{MCQCISD}	$\mathrm{TC}E_{\mathrm{B3LYP/6\text{-}31G^{*}}}$
5-hydroxy-α-tetralone	−537.689871	−537.746219	−536.841911	−536.848406	0.182735
6-hydroxy-α-tetralone	−537.693594	−537.750345	−536.844351	−536.850874	0.182729
7-hydroxy-α-tetralone	−537.689949	−537.746679	−536.841688	−536.848148	0.182553
8-hydroxy-α-tetralone	−537.705402	−537.761475	−536.853624	−536.860550	0.183002
5-hydroxy-*β*-tetralone	−537.682785	−537.740106	−536.836945	−536.843314	0.181900
6-hydroxy-*β*-tetralone	−537.684120	−537.741727	−536.837878	−536.844226	0.181852
7-hydroxy-*β*-tetralone	−537.684199	−537.741810	−536.838006	−536.844337	0.180390
8-hydroxy-*β*-tetralone	−537.683402	−537.740760	−536.837836	−536.844223	0.182107
α-tetralone	−462.447184	−462.494829	−461.685403	−461.689668	0.177571
β-tetralone	−462.440538	−462.489121	−461.681082	−461.685189	0.176749
benzene	−232.311529	−232.337565	−231.899673	−231.902529	0.101394
phenol	−307.555588	−307.59074	−307.057040	−307.062130	0.106438
carbon	−37.855989	−37.858574	−37.788011	−37.788422	0.0014162[c]
hydrogen	−0.502156	−0.502156	−0.499816	−0.499881	0.0014162[c]
oxygen	−75.085384	−75.091863	−74.991533	−74.992534	0.0014162[c]

[a] All energies are in a.u. (1 E_{H} = 2625.50184 kJ·mol^{-1}). [b] $\mathrm{TC}E_{\mathrm{B3LYP/6\text{-}31G^{*}}} = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{zp}} + \Delta_{0\mathrm{K}}^{298.15\mathrm{K}}E_{\mathrm{vib}}$. [c] Values corresponding to the translational energy of the atom at T = 298.15 K (E_{trans} = 3/2RT).

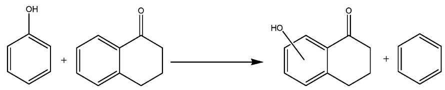
Table 7. Computed Estimates of the Standard Enthalpies of Formation in the Gas Phase at T = 298.15 K Obtained from Reactions 6 and 7 and from Atomization Reactions

	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$(g)/kJ·mol^{-1}							
	reactions 6 and 7				atomization reaction			
	DFT/B3LYP				DFT/B3LYP			
compd	6-311G**	cc-pVTZ	MC-UT	MC-QCISD	6-311G**	cc-pVTZ	MC-UT	MC-QCISD
5-hydroxy-α-tetralone	−270.4	−269.3	−271.7	−271.7	−147.3	−193.3	−260.0	−259.2
6-hydroxy-α-tetralone	−280.1	−280.1	−278.1	−278.2	−157.1	−204.2	−266.4	−265.7
7-hydroxy-α-tetralone	−271.0	−271.0	−271.6	−271.5	−147.9	−195.0	−259.8	−259.1
8-hydroxy-α-tetralone	−310.4	−308.6	−301.8	−302.9	−187.3	−232.7	−290.0	−290.4
5-hydroxy-*β*-tetralone	−249.2	−248.2	−250.0	−250.0	−130.8	−179.5	−249.1	−248.1
6-hydroxy-*β*-tetralone	−252.8	−252.6	−252.5	−252.6	−134.5	−183.8	−251.7	−250.6
7-hydroxy-*β*-tetralone	−256.8	−256.6	−256.7	−256.7	−138.5	−187.9	−255.9	−254.7
8-hydroxy-*β*-tetralone	−250.2	−249.3	−251.8	−251.9	−131.9	−180.6	−250.9	−249.9

by far greater than the energy associated with normal hydrogen bonds. So, also from the energetic point of view, a need for further stabilization mechanisms is evident. According to our previous analysis, these mechanisms necessarily involve electron delocalization (hyperconjugation) within the newly formed ring. This conjecture can, fortunately, be quantitatively tested within the context of NBO analysis.[30] We have analyzed the main changes in the donor−acceptor type interactions as the H bond became allowed. Even though simple perturbation theory is used to evaluate the stabilizing effects, we could at least identify the following changes that occur upon the hydrogen bond formation: 3.35 kcal·mol^{-1} to 28.26 kcal·mol^{-1} for the $\pi_{\mathrm{C8-C9}} \rightarrow \pi^{*}_{\mathrm{C1-O11}}$ interaction; 0.31 kcal·mol^{-1} to 3.39 kcal·mol^{-1} for $\pi_{\mathrm{C1-O11}} \rightarrow \pi^{*}_{\mathrm{C8-C9}}$; 1.88 kcal·mol^{-1} to 5.29 kcal·mol^{-1} for $\mathrm{n}\sigma_{\mathrm{O11}} \rightarrow \sigma^{*}_{\mathrm{C1-C9}}$, and 5.46 kcal·mol^{-1} to 12.95 kcal·mol^{-1} for $\mathrm{n}\pi_{\mathrm{O11}} \rightarrow \sigma^{*}_{\mathrm{C1-C9}}$. The energetic importance of these hyperconjugative interactions in stabilizing the conformer with the hydrogen bond is clearly a further corroboration of the fact that the enhanced stability of 8-hydroxy-α-tetralone is a consequence of both the hydrogen bond formation and very important hyperconjugative electronic delocalization phenomena.

The last observation we retain about the conformational behavior of these systems is the coplanarity between the O−H substituents and the benzenoid ring, which, as observed repeatedly in earlier work,[38−43] favors the extended electronic delocalization involving the benzenoid ring and the oxygen atom π lone electronic pair.

To estimate the enthalpies of formation of the systems from the calculated energies, we used the following homodesmotic reaction involving auxiliary systems whose thermochemical properties are well established experimentally[34,44,45] as well as atomization reactions



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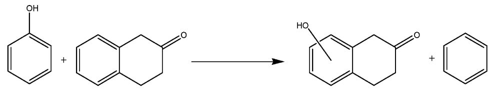

(7)

Total energies, identified by the subscripts B3LYP/6-311G**, B3LYP/cc-pVTZ, MCUT, and MCQCISD as well as thermal corrections, TC*E*/6-31G*, are reported in Table 6 for the studied compounds. The optimum geometries, the energies, and the thermal corrections for all of the auxiliary molecules have also been obtained using the same procedures as those described above.

The resulting estimates of the enthalpies of formation are provided in Table 7 for all of the molecules. The energetics of the studied systems deserve some considerations. In the first place, these systems can be clearly grouped, from an energetic point of view, into two distinct groups: those that contain the α-tetralone substract are clearly more stable than the remaining by a factor of about 10 kJ·mol^{-1}. This stability enhancement results from the conformational behavior, discussed earlier,[33] of the C−C(=O)−C moieties leading to different interactions between the carbonyl group (C=O) and the benzenoid ring and favoring the α position. We can furthermore observe that the

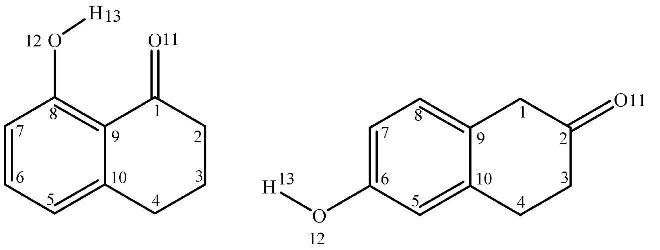

Figure 1. Atom numbering scheme for the geometric results of 8-hydroxy-α-tetralone and 6-hydroxy-β-tetralone, respectively.

8-hydroxy-α-tetralone isomer is much more stable, by about 30 kJ·mol^{-1}, than the remaining isomers within the same group. As stated above, this was expected on the basis of the peculiar intramolecular H bond formed between the −OH substituent and the carbonyl oxygen atom that allows the formation of a new six-membered ring structure, thus facilitating further circular electronic delocalization which, as is well known, is a considerable stabilizing factor. The computational estimates of the enthalpy of formation obtained by using the above homodesmotic reactions, either with the B3LYP energies or with the multicoefficient correlation energies, describe with moderate accuracy the available experimental data, the absolute deviations observed falling in the range of (10 to 12) kJ·mol^{-1}. However, when we use the atomization reactions to obtain the thermochemical estimates, we attain from the multicoefficient correlation energies results with an impressive accuracy whose absolute deviations do not exceed 3.2 kJ·mol^{-1} for the 5-hydroxy-α-tetralone and 2.4 kJ·mol^{-1} for 6-hydroxy-α-tetralone. We should be aware, however, of the presumably fortuitous nature of the enhancement of the atomization reaction results over those obtained from the homodesmotic reactions when both rely on the same accurate multicoefficient correlation energies. Nevertheless, the need for using very accurate energies remains evident when we observe the very large errors of the estimates of the enthalpies of formation obtained from atomization reactions and the B3LYP energies (Table 7).

In conclusion, our most accurate results, which attain the standard of "chemical accuracy", clearly show the importance of using accurately calculated energies in obtaining reliable estimates of thermochemical data and allow us to state the quality of the estimates presented for the systems that have not yet been studied experimentally as being of the same overall quality as the other ones.

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