



Experimental and computational study on the energetics of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (dibenzosuberane)

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ARTICLE INFO

Article history:

Received 6 October 2010

Accepted 13 October 2010

Available online 16 November 2010

Keywords:

Enthalpy

Combustion

Sublimation

Computational calculations

G3(MP2)//B3LYP

DHDFT

MC3BB

MC3MPW

10,11-Dihydro-5*H*-dibenzo[*a,d*]

cycloheptene

Dibenzosuberane

ABSTRACT

A study on the molecular structure and energetics of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (dibenzosuberane) was performed combining experimental calorimetric techniques and high level computational calculations. In the experimental work, the solid phase standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene was derived from its standard massic energy of combustion, at $T = 298.15$ K, measured by static bomb combustion calorimetry, in oxygen. The respective standard molar enthalpy of sublimation, at $T = 298.15$ K, was measured by Calvet microcalorimetry enabling the calculation of the standard molar enthalpy of formation (161.4 ± 3.7 kJ · mol^{−1}, in the gaseous phase, at $T = 298.15$ K. In addition, computational calculations were performed using the density functional theory with the B3LYP hybrid functional and extended basis sets in order to obtain the molecular structure of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene and that of related molecules. Estimates of the standard molar enthalpy of formation, in the gaseous phase, at $T = 298.15$ K, for 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene were performed using three different methods: G3(MP2)//B3LYP, MC3BB, and MC3MPW and appropriate homodesmotic reactions. Computational estimates are in very good agreement with the experimental value.

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1. Introduction

The compound 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (see figure 1) and its derivatives have received considerable attention over the years from the scientific community because a variety of biologically and pharmacologically active compounds involve this tricyclic substructure [1]. These compounds have been reported as being antidepressants [2], the most well known being amitriptyline (3-(10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5-ylidene)-*N,N*-dimethyl-1-propanamine) [3]. Dizocilpine (5-methyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5,10-imine), also known as MK-801, displays potent anticonvulsant and neuroprotective properties [4–7].

A large number of natural alkaloids which possess a dibenzo[*a,d*]cycloheptene ring system, such as isopavine and thal-isopavine, have shown potent and varied biological activity [8].

Due to the important applications of the derivatives of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene knowledge of their structure and energetics is highly needed. Experimental studies on the molecular structure of compounds with the dibenzo[*a,d*]cycloheptene structure found that these are non-planar molecules [9].

There are values reported by Perisanu and his coworkers of the standard molar enthalpy of formation in the condensed phase for some dibenzocycloheptane ketones [10], some dibenzoannelated cyclooctane ketones [11] and dibenzoannelated cycloalkanol [12]. Verevkin reported an experimental thermochemical study of the related carbonyl compound dibenzosuberone as part of the study of aromatic ketones [13].

In the present work, we report a combined experimental and computational study on the energetics of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene. From the experimental side, the standard molar enthalpy of formation of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene, in the solid phase, at $T = 298.15$ K, was derived from its standard massic energy of combustion measured by static bomb combustion calorimetry, in oxygen. The respective standard molar enthalpy of sublimation was measured by Calvet microcalorimetry and enabled the calculation of the standard molar enthalpy of formation in the gaseous phase, at $T = 298.15$ K. On

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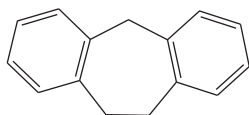


FIGURE 1. Structural formula of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene.

the computational side the molecular structure of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene and that of some related molecules were fully optimized using the density functional theory with the B3LYP functional and the 6-31G* and 6-311G** extended basis sets. We have further carried out energy calculations using the G3(MP2)//B3LYP composite method and two implementations of the Doubly Hybrid Density Functional Theory (DHDFT): the multi-coefficient three-parameter Becke88–Becke95 (MC3BB) method and multi-coefficient three-parameter modified Perdew–Wang (MC3MPW) method, which in conjunction with appropriate reactions allowed us to obtain estimates of the standard molar enthalpy of formation of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene, in the gaseous phase, at $T = 298.15$ K.

2. Experimental

2.1. Material and purity control

The 10,11-dihydro-5H-dibenzo[a,d]cycloheptene [CAS 833-48-7] was obtained commercially from Aldrich Chemical Co. with the assigned mass fraction of purity of 0.996 determined by gas-liquid chromatography. This compound was further purified by repeated vacuum sublimation before the calorimetric experiments.

The final purity of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene was assessed by differential scanning calorimetry (DSC) analysis, using the fractional fusion technique [14]. The DSC experiments were performed with a Setaram DSC 141 calorimeter. The samples were hermetically sealed in stainless steel crucibles and a heating rate of $1.67 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$ was used. The DSC thermograms did not show any transition phases between $T = 298.15$ K and the fusion temperature of the compound. The power scale of the calorimeter was calibrated with high purity indium (mass fraction > 0.99999) and its temperature scale was calibrated by measuring the melting temperature of the following three high purity reference materials [15]: naphthalene, benzoic acid, and indium.

The compositional purity of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene and the completeness of the combustion process were confirmed through the carbon dioxide recovery ratio after the combustion calorimetric experiment (see Section 2.2). The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample was: (1.0003 ± 0.0004) where the uncertainty is the standard deviation of the mean of five carbon dioxide recoveries.

2.2. Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter in a twin valve bomb, type 1108, from the Parr Instrument Company. Since the apparatus and the technique have been described [16,17], only a brief description will be given here. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid BDH Thermochemical Standard, batch 69376/01, certificated in Manchester University, having a massic energy of combustion of $\Delta_c u = -(26435.1 \pm 3.5) \text{ J} \cdot \text{g}^{-1}$, under certificate conditions. Calibration experiments were carried out in oxygen at the pressure of 3.04 MPa in the presence of 1.00 cm^3 of deionized water added to the bomb. One set of seven calibration experiments was performed leading to the value of the energy

equivalent of the calorimeter: $\varepsilon_{\text{cal}} = (16005.0 \pm 2.0) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

For all combustion experiments of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene, the samples, in the pellet form, were ignited at $T = (298.150 \pm 0.001) \text{ K}$, in oxygen, at a pressure of 3.04 MPa, with a volume of deionized water of 1.00 cm^3 added to the bomb.

The density of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene was estimated from the mass and the dimensions of the pellets used in the combustion experiments: $\rho = 0.93 \text{ g} \cdot \text{cm}^{-3}$.

The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, the standard massic energy of combustion used was $\Delta_c u^0 = -16,240 \text{ J} \cdot \text{g}^{-1}$: [18] this value was previously confirmed in our laboratory. The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [19], for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$ from $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance was made for that formed from the cotton thread fuse. An estimated pressure coefficient of massic 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 [20], was assumed. The massic energy of combustion $\Delta_c u^0$ was calculated by the procedure given by Hubbard *et al.* [21]. The atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005 [22].

2.3. Microcalorimetry calvet

The standard molar enthalpy of sublimation of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene was measured using the “vacuum sublimation” drop microcalorimetric method [23]. Samples, about 3 mg of the solid compound, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter (Calvet High Temperature Microcalorimeter, SETARAM HT 1000) held at a convenient temperature T , and then removed from the hot zone by vacuum sublimation. An empty capillary tube was dropped in the reference calorimetric cell, simultaneously. 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, to within $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells.

The microcalorimeter was calibrated *in situ* performing sublimation experiments with naphthalene following the same procedure as the one described for dibenzosuberane and using the reported standard molar enthalpy of sublimation of naphthalene $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (72.600 \pm 0.600) \text{ kJ} \cdot \text{mol}^{-1}$ [24] a primary reference material. Accuracy tests were performed with benzoic acid $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (89.700 \pm 1.000) \text{ kJ} \cdot \text{mol}^{-1}$ [24].

3. Computational details

The geometry of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene and of all the other molecules used in this study were fully optimized using density functional theory (DFT) based on the Becke 3-parameter hybrid exchange [25] and Lee *et al.* [26] correlation density functional (B3LYP) and the Pople split-valence 6-31G* extended basis [27]. The optimum structures so obtained were further certified as true minima by constructing and diagonalizing the corresponding Hessian matrix, this procedure providing also the thermal energy correction terms necessary to obtain enthalpy values at $T = 298.15 \text{ K}$. We have further refined the optimum structures by reoptimizing them using the same methodology but now with the Pople split-valence 6-311G** extended basis set [28].

These final optimized structures were then used to perform single point energy calculations based on more accurate correlated computational techniques of the DHDFT type: the multi-coefficient three-parameter Becke88–Becke95 (MC3BB) method and multi-coefficient three-parameter modified Perdew–Wang (MC3MPW) method [29]. These methods involve combining multi-coefficient correlated methods (MCCM) [30] with hybrid density functional theory (HDFT) techniques [25,26,31] and have been observed to have excellent cost-to-performance ratios [29]. In addition, we have also conducted calculations using the G3(MP2)//B3LYP method [32].

All calculations were performed with the Gaussian 03 series of programs [33]. The DHDFT calculations were conducted by using the program using the MLGAUSS program version 2.0 [34], which relies on the Gaussian 03 code.

4. Results

4.1. Experimental results

The molar fraction of purity of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene, its temperature of fusion (observed at the onset of the calorimetric peaks) and enthalpy of fusion were computed from the DSC thermograms: $T_{\text{fus}} = (348.03 \pm 0.11) \text{ K}$, $\Delta_{\text{cr}}^{\text{H}} H_{\text{m}}^{\circ}(T_{\text{fus}}) = (23.33 \pm 0.35) \text{ kJ} \cdot \text{mol}^{-1}$ and $w = (99.86 \pm 0.02)$. The uncertainties assigned to the results are twice the standard deviation of the mean of six independent runs.

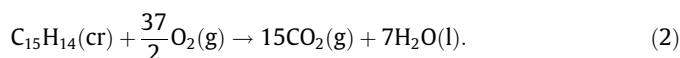
Detailed results for the combustion experiments of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene are given in table 1. The symbols in this table have the same meaning as in reference [21]. As samples were ignited at $T = 298.15 \text{ K}$,

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

where $\Delta U(\text{IBP})$ is the energy associated with the isothermal bomb process, $c_p(\text{H}_2\text{O}, \text{l})$ is the specific heat capacity of liquid water, $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, ε_{f} is the energy of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature increase raise calculated using the program Labtermo [35] and ΔU_{ign} is the energy of ignition.

The individual results of the massic energies of combustion, $\Delta_c u^{\circ}$, at $T = 298.15 \text{ K}$, for all combustion experiments, together with the mean value and its standard deviation, are given in table 1. The

values of $\Delta_c u^{\circ}$ are referred to the idealized combustion reaction represented by the following equation:



From the mean value for $\Delta_c u^{\circ}$, we have derived the values for the standard molar energy of combustion, $\Delta_c U_{\text{m}}^{\circ}(\text{l}) = -7952.6 \pm 2.4 \text{ kJ} \cdot \text{mol}^{-1}$, and for the standard molar enthalpy of combustion, $\Delta_c H_{\text{m}}^{\circ}(\text{l}) = -(7961.3 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$. In accordance with customary thermochemical practice [36], the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{cr}) = 57.8 \pm 3.1 \text{ kJ} \cdot \text{mol}^{-1}$ from $\Delta_c H_{\text{m}}^{\circ}(\text{cr})$, the standard molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$, at $T = 298.15 \text{ K}$, were taken, respectively as, $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$ [37] and $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ [37].

The standard molar enthalpy of sublimation of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene was measured by Calvet microcalorimetry. From six independent sublimation experiments performed, at $T = 366 \text{ K}$, a mean experimental value $\Delta_{\text{cr}}^{\text{g},T} H_{\text{m}}^{\circ} = (119.3 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ was observed. From this value, the standard molar enthalpy of sublimation, at $T = 298.15 \text{ K}$, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = 103.6 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$, was derived using the correction term $\Delta_{298.15 \text{ K}}^T H_{\text{m}}^{\circ}$, which was calculated as follows (equation (3)):

$$\Delta_{298.15 \text{ K}}^T H_{\text{m}}^{\circ}(\text{g}) = \int_{298.15 \text{ K}}^T C_{p,\text{m}}^{\circ}(\text{g}) dT, \quad (3)$$

where T is the temperature of the microcalorimeter Calvet and $C_{p,\text{m}}^{\circ}$ is the molar heat capacity of the gaseous compound. The heat capacity and its temperature dependence

$$C_{p,\text{m}}^{\circ}(\text{g})/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = -0.000522(T/\text{K})^2 + 1.118(T/\text{K}) - 82.137 \quad (4)$$

were derived from statistical thermodynamics using the B3LYP/6-31G* vibrational frequencies calculations. The uncertainty associated to the value of $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K})$ is twice the standard deviation of the mean of the six independent runs and includes the uncertainty in the calibration.

Combining the value of the standard enthalpy of formation in the solid phase, $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{cr}) = 57.8 \pm 3.1 \text{ kJ} \cdot \text{mol}^{-1}$, with the value of the standard molar enthalpy of sublimation, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (103.6 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$, we have calculated the standard molar

TABLE 1
Results of the combustion experiments of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene.

| Experiment no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|----------|----------|----------|----------|----------|----------|----------|----------|
| $m(\text{CO}_2, \text{total})/\text{g}$ | 1.97043 | | | 1.77223 | | 1.64085 | | 2.36376 |
| $m(\text{cpd})/\text{g}$ | 0.57872 | 0.55567 | 0.51594 | 0.52042 | 0.44790 | 0.48168 | 0.53986 | 0.69435 |
| $m(\text{fuse})/\text{g}$ | 0.00244 | 0.00276 | 0.00266 | 0.00238 | 0.00237 | 0.00253 | 0.00294 | 0.00269 |
| $\Delta T_{\text{ad}}/\text{K}$ | 1.48215 | 1.42433 | 1.32202 | 1.33307 | 1.14813 | 1.23470 | 1.38380 | 1.77820 |
| $\varepsilon_{\text{f}}/(\text{J} \cdot \text{K}^{-1})$ | 16.00 | 15.84 | 15.73 | 15.74 | 15.79 | 15.88 | 15.87 | 16.34 |
| $\Delta m(\text{H}_2\text{O})/\text{g}$ | −0.1 | −0.1 | 0.8 | −0.1 | 0.1 | 0.2 | 0.1 | 0.0 |
| $-\Delta U(\text{IBP})/\text{J}$ | 23744.24 | 22817.84 | 21183.59 | 21355.56 | 18393.86 | 19781.49 | 22163.93 | 28481.15 |
| $-\Delta U(\text{HNO}_3)/\text{J}$ | 0.87 | 10.03 | 9.43 | 9.25 | 11.27 | 12.06 | 1.79 | 1.18 |
| $-\Delta U(\text{carbon})/\text{J}$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $\Delta U(\text{ignition})/\text{J}$ | 0.67 | 0.53 | 0.56 | 0.65 | 0.57 | 0.52 | 0.52 | 0.53 |
| $-\Delta U_{\Sigma}/\text{J}$ | 12.29 | 11.78 | 10.84 | 10.93 | 9.26 | 10.04 | 11.39 | 15.15 |
| $-\Delta U(\text{fuse})/\text{J}$ | 39.63 | 44.82 | 43.20 | 38.65 | 38.49 | 41.09 | 47.75 | 43.69 |
| $-\Delta_c u^{\circ}/(\text{J} \cdot \text{g}^{-1})$ | 40937.67 | 40943.74 | 40935.22 | 40922.20 | 40935.12 | 40936.51 | 40942.10 | 40931.99 |
| $-(\Delta_c u^{\circ}) = 40935.6 \pm 2.3 (\text{J} \cdot \text{g}^{-1} (0.0056\%))$ | | | | | | | | |

$m(\text{CO}_2, \text{total})$ is the total mass of CO_2 formed in the experiment; $m(\text{compound})$ is the mass of compound burnt in the experiment; $m(\text{fuse})$ is the mass of fuse (cotton) used in the experiment; ΔT_{ad} is the corrected temperature rise; ε_{f} is the energy equivalent of contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{IBP})$ includes the ignition energy, $\Delta U(\text{ignition})$; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{carbon})$ is the energy correction for carbon formation; ΔU_{Σ} is the energy correction to the standard state; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta_c u^{\circ}$ is the standard massic energy of combustion.

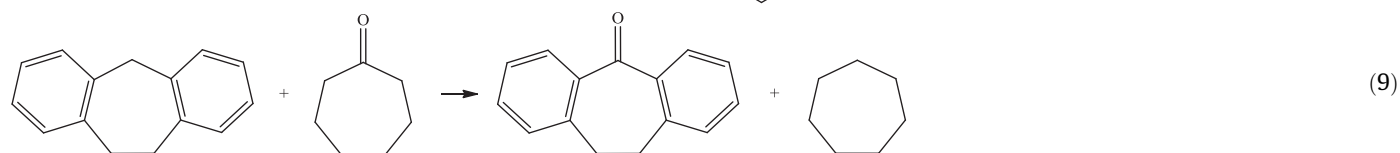
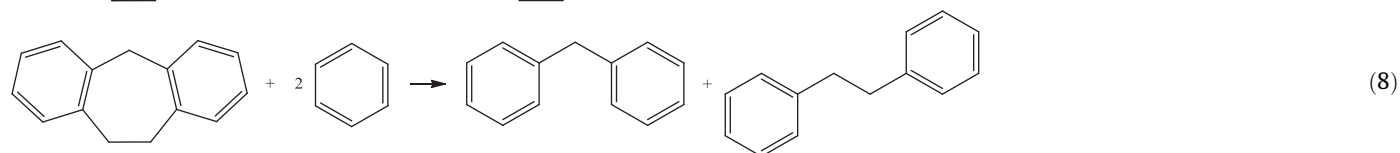
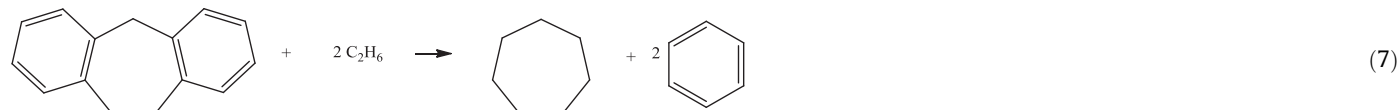
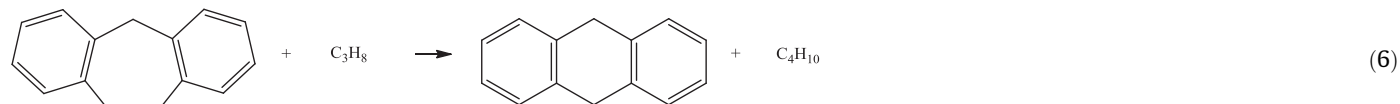
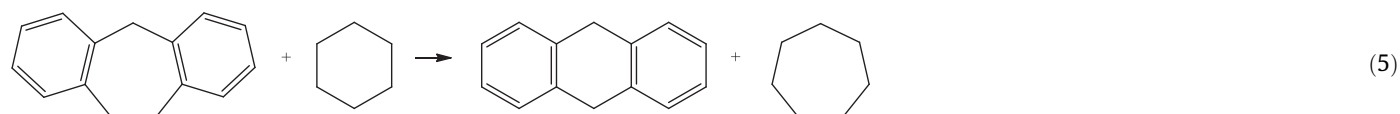
enthalpy of formation of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene, in the gaseous phase, at $T = 298.15$ K, $\Delta_f H_m^\circ(\text{g}) = (161.4 \pm 3.7) \text{ kJ} \cdot \text{mol}^{-1}$.

4.2. Computational results

The most stable molecular structure of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene was obtained using DFT with the B3LYP functional and the 6-31G* and 6-311G** basis sets. Figure 2 shows four different views of the optimized geometry obtained with the more extended basis set. We can see from figure 2(b) that dibenzosuberane has clearly a non-planar geometry with a “butterfly” shape. The angle between the two terminal rings is of

central ring has only six carbon atoms, and fluorene, where the central ring has only five carbon atoms, in order to establish a comparison with the structure of dibenzosuberane. 9,10-Dihydroanthracene, similarly to what we found for dibenzosuberane, presents a non-planar geometry with a “butterfly” shape (figure 3). However, the angle between the two terminal rings is higher: 142.1° . Fluorene is a planar molecule (see figure 4). As the number of methylene fragments decrease the molecules became more planar.

The standard molar enthalpy of formation of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene in the gaseous phase, at $T = 298.15$ K, has been estimated from the G3(MP2)//B3LYP and the MC3BB and MC3MPW calculations using the following equations:



119.2° . In this compound the cycloheptane ring has a half-chair or sofa conformation (see figure 2(d)). The steric repulsions between the hydrogen atoms of the two $-\text{CH}_2-$ fragments in the cycloheptane ring are minimized by the staggered arrangement of the hydrogen atoms (see figure 2(d)).

Freeman *et al.* [38] used high level theoretical calculations to perform a conformational analysis for cycloheptane and some oxa-derivatives. These calculations showed that cycloheptane has two minima, the twist chair and the boat conformers, and three transition states. The twist chair conformer was found to be lower in energy than the boat conformer by about $14 \text{ kJ} \cdot \text{mol}^{-1}$. We have also fully optimized the geometry of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene at the B3LYP/6-31G* level, with the cycloheptane ring having a boat-like conformation. The vibrational analysis revealed this conformation to be a first order saddle-point with just one imaginary frequency, rather than a minimum. Also, the energy of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene with the cycloheptane having a boat-like structure was found to be about $12 \text{ kJ} \cdot \text{mol}^{-1}$ (B3LYP/6-31G* electronic energy difference without any zero-point or thermal energy correction) higher in energy than the conformation described above, where the cycloheptane ring has a half chair or sofa conformation.

We have further optimized the geometry at the B3LYP/6-311G** level of the related molecules: 9,10-dihydroanthracene, where the

These reactions were chosen on the basis of available experimental data for all the auxiliary molecules involved in the reactions. It must be noted also that these reactions were chosen to be, at least, of the isodesmic type so that the correlation errors are likely to largely cancel in reactants and products thus leading to reliable estimates of the reaction enthalpies. These were combined with the experimental standard molar enthalpies of formation of all the intervening molecules, with the exception of that of dibenzosuberane, to obtain its standard molar enthalpy of formation in the gaseous phase, at $T = 298.15$ K. The results are presented in table 2.

The obtained MC3BB and MC3MPW electronic energies at $T = 0$ K, the B3LYP/6-31G* thermal corrections from $T = 0$ K to $T = 298.15$ K and the G3(MP2)//B3LYP absolute enthalpies at $T = 298.15$ K for 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene and the auxiliary molecules used in this study are presented in Supplementary data material in Table S1 together with the respective experimental values of the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K. These values were all taken from Pedley's compendium [39] except for benzene [40], dibenzosuberone [13] and diphenylmethane [40]. The computational estimates obtained using equations (5) to (8) are in good agreement with the experimental value with a maximum deviation of $9.0 \text{ kJ} \cdot \text{mol}^{-1}$. Using equation (9) the computational estimates are very different from the experimental value. This estimates were

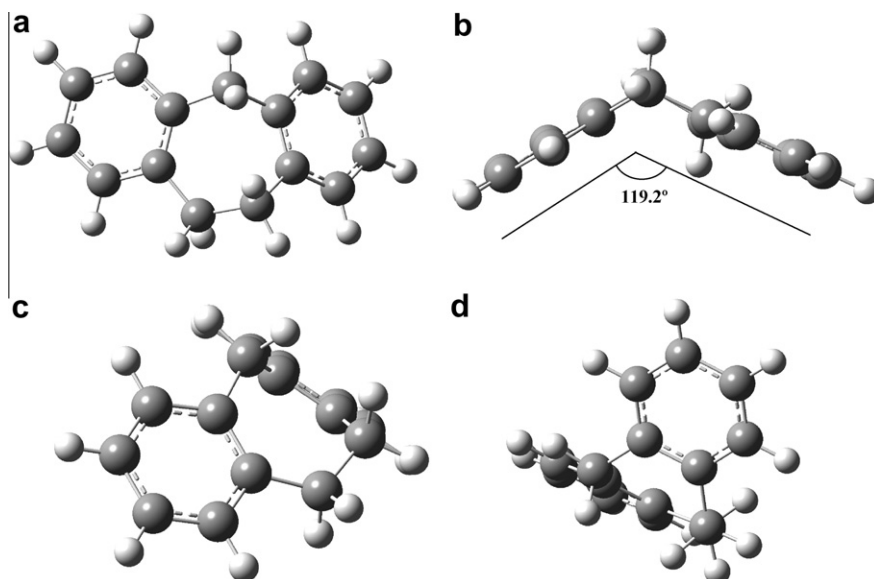


FIGURE 2. Different views of the 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene optimized B3LYP/6-311G** geometry.

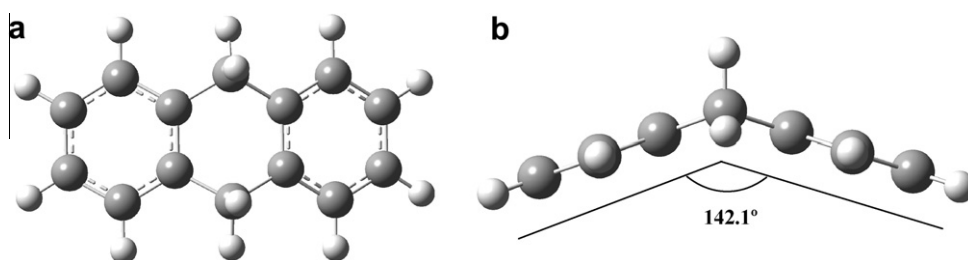


FIGURE 3. Different views of the 9,10-dihydroanthracene optimized B3LYP/6-311G** geometry.

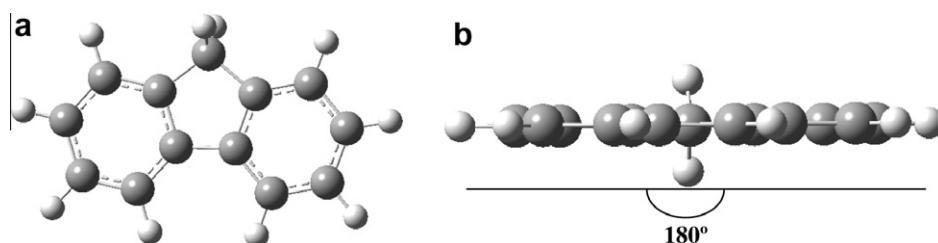


FIGURE 4. Different views of the fluorene optimized B3LYP/6-311G** geometry.

TABLE 2

Computational estimates of the standard molar enthalpy of formation of 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene, in the gaseous phase, at $T = 298.15$ K.

| Equation | $\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$ | | |
|----------|--|----------------------------|----------------------------|
| | G3(MP2)//B3LYP | MC3BB | MC3MPW |
| | 154.8 (6.6) | 156.1 (5.3) | 157.6 (3.8) |
| | 154.7 (6.7) | 158.2 (3.2) | 158.9 (2.5) |
| | 152.4 (9.0) | 163.8 (−2.4) | 158.5 (2.9) |
| | 161.5 (−0.1) | 154.9 (6.5) | 158.8 (2.6) |
| | 183.3 ^a (−21.9) | 186.9 ^a (−25.5) | 189.8 ^a (−28.4) |
| | 161.5 ^b (−0.1) | 165.1 ^b (−3.7) | 168.0 ^b (−6.6) |

Enthalpic differences between the experimental and computed values are given in parentheses.

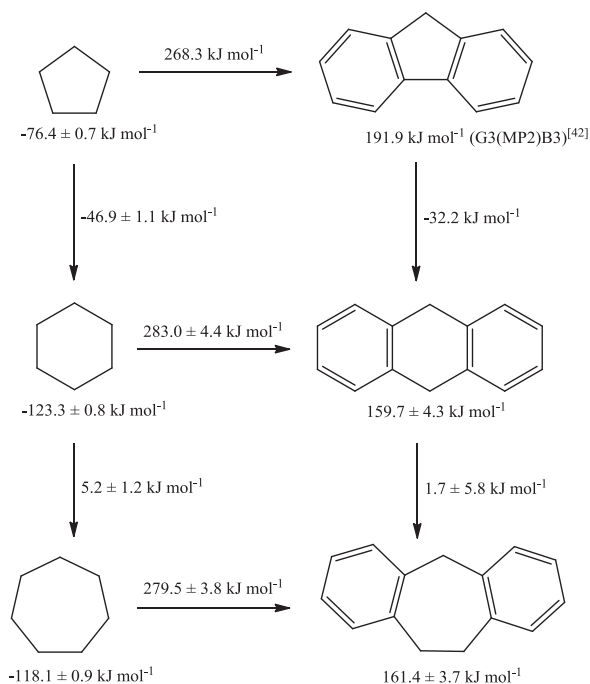
^a Using the $\Delta_f H_m^\circ(\text{g})$ for cycloheptanone of $-247.5 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1}$ [39].

^b Using the $\Delta_f H_m^\circ(\text{g})$ for cycloheptanone of $-225.7 \text{ kJ} \cdot \text{mol}^{-1}$ [41].

obtained using the recommended value from Pedley's compendium [39] for the standard molar enthalpy of formation of cycloheptanone of $-247.5 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1}$. However using the G3(MP2)//B3LYP estimated value of $-225.7 \text{ kJ} \cdot \text{mol}^{-1}$ [41], the computational estimates show very good agreement with the experimental value with a maximum deviation of only $6.6 \text{ kJ} \cdot \text{mol}^{-1}$. This fact supports both the experimental standard molar enthalpy of formation of 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene obtained in this work and the value obtained, in a previous work [41], for cycloheptanone using the G3(MP2)//B3LYP calculations.

5. Discussion

The experimental enthalpic increment for the introduction of two benzene rings in cycloheptane is $(279.5 \pm 3.8) \text{ kJ} \cdot \text{mol}^{-1}$. This



SCHEME 1. Enthalpic increments of the introduction of two benzene rings in the cycloalkane rings.

enthalpic increment is compared in [scheme 1](#) with those calculated for the entrance of the same number of benzene rings in the cyclohexane and cyclopentane rings. These were calculated from experimental values taken from Pedley's compendium [39] except for fluorene. Recently, Roux *et al.* [40] recommended the value of $(176.7 \pm 3.1) \text{ kJ} \cdot \text{mol}^{-1}$ for the standard molar enthalpy of formation of fluorene. As there were some doubts about this value, Freitas *et al.* [42] performed G3(MP2)//B3LYP calculations and suggested that the value $191.1 \text{ kJ} \cdot \text{mol}^{-1}$ should be used as the standard molar enthalpy of fluorene. The enthalpic increment for the entrance of two benzene rings in cycloheptane is similar to the enthalpic increment for the same entrance in the cyclohexane ring but for cyclopentane is about $10 \text{ kJ} \cdot \text{mol}^{-1}$ lower.

6. Conclusions

A combined experimental and computational study was performed and the standard molar enthalpy of formation in the gaseous phase of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene was derived: $(161.4 \pm 3.7) \text{ kJ} \cdot \text{mol}^{-1}$. The experimental result determined in the present work is in good agreement with the values estimated using the G3(MP2)//B3LYP composite method and two implementations of the Doubly Hybrid Density Functional Theory (DHDFT): the multi-coefficient three-parameter Becke88–Becke95 (MC3BB) method and multi-coefficient three-parameter modified Perdew–Wang (MC3MPW) method.

Acknowledgements

Thanks are due to Fundação para a Ciência e a Tecnologia, FCT, Lisbon, Portugal, and to FEDER for financial support to Centro de Investigação em Química, University of Porto. M.S. Miranda thanks FCT for the award of the postdoctoral scholarship (BPD/5594/2001) and for the financial support under the frame of the Ciência 2008 program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jct.2010.10.009](https://doi.org/10.1016/j.jct.2010.10.009).

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