

The structure and thermochemistry of 3:4,5:6-dibenzo-2-hydroxymethylene-cyclohepta-3,5-dienone (**1**) and some related compounds

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Received: 8 May 2006 / Accepted: 21 August 2006

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Abstract Condensed and gas phase enthalpies of formation of 3:4,5:6-dibenzo-2-hydroxymethylene-cyclohepta-3,5-dienone (**1**, $\Delta_f H_m^\circ = -199.1 \pm 16.4$ and -70.5 ± 20.5 kJ mol⁻¹) and 3,4,6,7-dibenzobicyclo[3.2.1]nona-3,6-dien-2-one (**2**, $\Delta_f H_m^\circ = -79.7 \pm 22.9$ and 20.1 ± 23.1 kJ mol⁻¹) are reported. Sublimation enthalpies at $T = 298.15$ K for these compounds were evaluated by combining the fusion enthalpies at $T = 298.15$ K (**1** (12.5 ± 1.8 kJ mol⁻¹); **2** (5.3 ± 1.7 kJ mol⁻¹)) adjusted from DSC measurements at the melting temperature (**1** ($T_{\text{fus}} = 357.7$ K, 16.9 ± 1.3 kJ mol⁻¹); **2** ($T_{\text{fus}} = 383.3$ K, 10.9 ± 0.1 kJ mol⁻¹)) with the vaporization enthalpies at $T = 298.15$ K (**1** (116.1 ± 12.1 kJ mol⁻¹); **2** (94.5 ± 2.2 kJ mol⁻¹)) measured by correlation-gas chromatography. The vaporization enthalpies of benzoin (98.5 ± 12.5 kJ mol⁻¹) and 7-heptadecanone (94.5 ± 1.8 kJ mol⁻¹) at $T = 298.15$ K and the fusion enthalpy of phenyl salicylate ($T_{\text{fus}} = 312.7$ K, 18.4 ± 0.5 kJ mol⁻¹) were also determined for the correlations. The crystal structure of **1** was determined by

X-ray crystallography. Compound **1** exists entirely in the enol form and resembles the crystal structure found for benzoylacetone.

Keywords Thermochemistry · Sublimation enthalpy · Vaporization enthalpy · Fusion enthalpy · Crystal structure of enol · Enthalpy of formation

Introduction

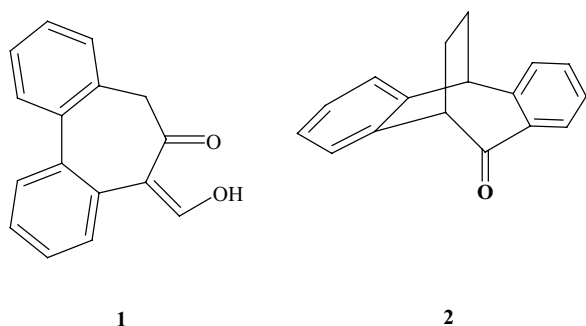
In previous work, the thermochemical properties of some dibenzocycloalkane derivatives have been reported [1–3]. This paper continues the thermochemical investigation of some dibenzoannulated cyclo- and bicycloalkanones, 3:4,5:6-dibenzo-2-hydroxymethylene-cyclohepta-3,5-dienone (**1**) and 3,4,6,7-dibenzobicyclo[3.2.1]nona-3,6-dien-2-one (**2**). The vaporization enthalpy of 7-heptadecanone and benzoin and the fusion enthalpy of phenyl salicylate are also reported. Benzoin and phenyl salicylate were used as auxiliary standards in the determination of the vaporization and sublimation enthalpies of compounds **1** and **2**. In addition, the crystal structure of **1** has also been determined. Compound **1** is an example of a compound that can exist in two tautomeric forms. In contrast to the 750 crystal structures of beta-enones currently available in the Cambridge database [4], only one crystal structure of a α -hydroxymethylene-enol is available, that of a complex natural product **3**, a phytotoxin isolated from culture filtrates of *Phoma batae* Fr., the causal fungus of leaf spot disease of sugar beet [5]. The crystal structure of **1** is a simpler example of this structural motif. The bonding observed in the enolic portion of **1** is similar to that found in the crystal structures of other beta-enones.

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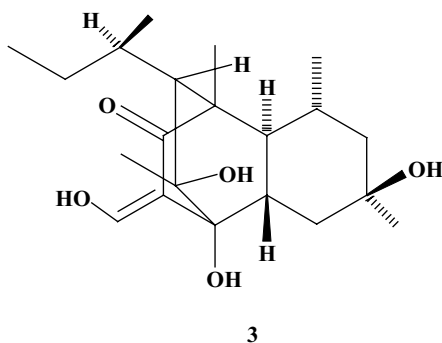
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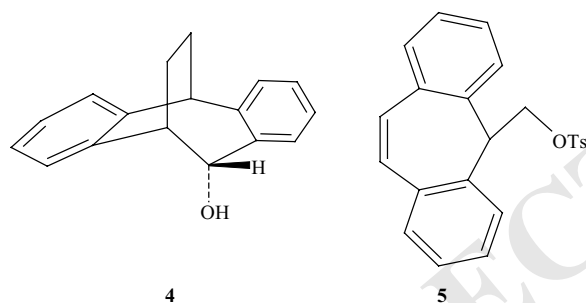
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Scheme 1



Scheme 2



Scheme 3

61 Experimental

62 Synthesis and purification

63 Compound **1** –(5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-one) was prepared as previously reported [6], by the condensation of 3:4,5:6 dibenzocycloheptanone with ethyl formate, in the presence of sodium methoxide. A yellow oily product was first extracted with ether, was washed with water, dried, and evaporated. The resulting hydroxy-methylene ketone **1** isolated was recrystallized from ethanol (mp 88–90°C). The ¹H NMR and IR data suggested the existence of only one tautomeric form, namely the hydroxy-methylene ketone **1**.

73 2:3,6:7-Dibenzobicyclo[3.2.2]nona-2,6-dien-4-one (**2**) was obtained by the procedure reported previously [7], consisting of CrO₃/pyridine oxidation of the *endo* alcohol **4**,

76 which is the main product of NaOAc buffered acetolysis of 77 dibenzocycloheptenyl-ethyl-β-tosylate (**5**) [7]. The ethereal 78 layer resulting from extraction was repeatedly washed, 79 then dried, and evaporated. Ketone (**2**) obtained in this 80 way was purified by recrystallization from methanol (mp 81 113–114°C).

82 Samples of both compounds were analyzed by gas chromatography and found to be over 99.9% pure. 83

Crystallography

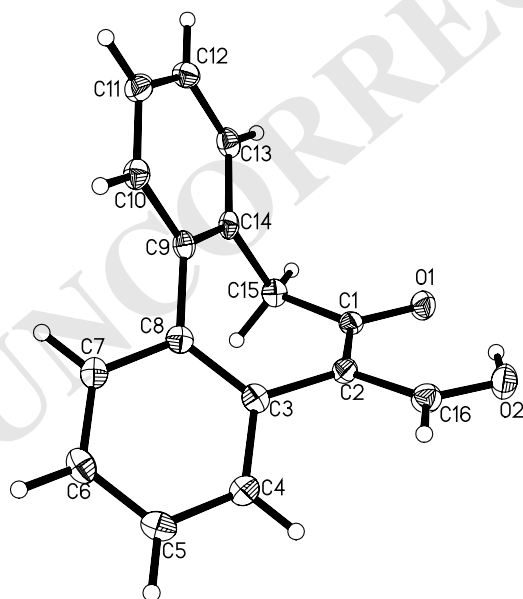
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85 Colorless crystals were grown by slow evaporation from 86 ethyl acetate–hexane solution at ambient temperature. 87 A crystal with dimensions 0.25 × 0.10 × 0.05 mm³ was 88 mounted on a glass fiber in a random orientation. Preliminary 89 examination and data collection was performed using a 90 Bruker APEX II charge coupled device (CCD) detector 91 system single crystal X-ray diffractometer using graphite 92 monochromatic Mo Kα radiation (λ = 0.71073 Å) equipped 93 with a sealed tube X-ray source at T = 100 K using an 94 Oxford Cryostream LT device. Preliminary unit cell constants 95 were determined with a set of 36 narrow frames (0.5° 96 in ω) scans. The intensity dataset was collected consisted of 97 φ and ω scans at a crystal to detector distance of 4.00 cm. 98 The double pass method of scanning was used to exclude 99 any noise. The collected frames were integrated using an 100 orientation matrix determined from the narrow frame scans. 101 APEX II and SAINT software packages (Bruker Analytical 102 X-ray, Madison, WI, 2005) were used for data collection and 103 data integration. Analysis of the integrated data did not show 104 any decay. Final cell constants were determined by a global 105 refinement of xyz centroids of 4779 reflections (θ < 26.4°). 106 Collected data were corrected for systematic errors using 107 SADABS [8] based on the Laue symmetry using equivalent 108 reflections. The integration process yielded 13,062 reflections, 109 of which 2395 were independent reflections.

110 Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement were carried out using the SHELXTL software package [9]. The structure was solved by direct methods and refined successfully in the space group *P*2₁/*c*. Full matrix least-squares refinement was carried out by minimizing Σw(F_o² – F_c²)². The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding model (AFIX m3). The final residual values were R(F) = 3.9% for 1751 observed reflections [I > 2σ(I)] and wR(F²) = 10.2%; s = 1.0 for all data. Figure 1 shows the projection view of the molecule with non-hydrogen atoms, represented by 50% probability ellipsoids, and the atom labeling. 123

124 Complete listings of the atomic coordinates for the 125 non-hydrogen atoms and the geometrical parameters, positional and isotropic displacement coefficients for hydro- 126

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	C ₁₆ H ₁₂ O ₂
Formula weight	236.26
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	12.4486(10)
<i>b</i> (Å)	14.2194(10)
<i>c</i> (Å)	6.4140(5)
α (°)	90
β (°)	98.968(4)
γ (°)	90
Volume (Å ³)	1121.47(15)
<i>Z</i>	4
Density (calculated) (Mg m ⁻³)	1.399
Absorption coefficient (mm ⁻¹)	0.091
<i>F</i> (0 0 0)	496
Crystal size (mm ³)	0.25 × 0.10 × 0.05
Theta range for data collection (°)	2.87 to 26.39
Index ranges	−15 ≤ <i>h</i> ≤ 15, −17 ≤ <i>k</i> ≤ 17, −7 ≤ <i>l</i> ≤ 5
Reflections collected	13062
Independent reflections	2285 [<i>R</i> _{int} = 0.043]
Completeness to theta = 26.39°	99.7%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.9954 and 0.9775
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2285/0/163
Goodness-of-fit on <i>F</i> ²	1.008
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0392, <i>wR</i> ₂ = 0.0903
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0592, <i>wR</i> ₂ = 0.1017
Largest differential peak and hole	0.421 and −0.362 (e Å ⁻³)

**Fig. 1** The X-ray crystal structure of 3:4,5:6-dibenzo-2-hydroxymethylene-cyclohepta-3,5-dienone (**1**)

gen atoms, and anisotropic displacement coefficients for the non-hydrogen atoms are deposited with the Cambridge Crystallographic Data Center (CCDC #XXX).

Fusion enthalpies

Fusion enthalpies were measured on a Perkin-Elmer DSC 7 in sealed aluminum cells. The cells were weighed before and after fusion to determine whether any mass was lost. No mass loss was observed. The instrument was calibrated using indium metal. Temperature was scanned at 5 K/min. The results are reported in Table 2. Fusion enthalpies measured at the melting temperature were adjusted to $T = 298.15$ K using Eq. 1 and the heat capacities listed in Table 2 [10]. Condensed phase heat capacities ($C_p(l)$ and $C_p(cr)$, column 5, Table 2) at $T = 298.15$ K were estimated by group additivity [11].

$$\begin{aligned} \Delta_{cr}^1 H_m(298.15 \text{ K}) (\text{kJ mol}^{-1}) \\ = \Delta_{cr}^1 H_m(T_{fus}) + [0.15 C_p(cr) - 0.26 C_p(l) \\ - 9.83 \text{ J K}^{-1} \text{ mol}^{-1}](T_{fus} - 298.15 \text{ K})/1000; \end{aligned} \quad (1)$$

Vaporization enthalpies

Enthalpies of transfer from the stationary phase of the column to the vapor, $\Delta_{sln}^g H_m(T_m)$, were measured by gas chromatography. The temperature T_m refers to the mean temperature of measurement. Values of $\Delta_{sln}^g H_m(T_m)$ were calculated as the product of the gas constant, R , and the slope of the line obtained by plotting of the natural logarithm of reciprocal corrected retention time versus $1/T$ (K⁻¹) as previously reported [12]. Experimental retention times are provided in Tables 3 and 4. The enthalpies of transfer were then correlated against literature vaporization enthalpies evaluated at $T = 298.15$ K. Literature vaporization enthalpies at $T = 298.15$ K used in the correlations are summarized in Table 5. The vaporization enthalpies were adjusted to $T = 298.15$ K when necessary using Eq. (2). The vaporization enthalpies of two solids, phenyl salicylate and 4-hydroxyacetophenone, were calculated by difference from the sublimation [13, 14] and fusion enthalpies, both adjusted to $T = 298.15$ K. Temperature adjustments were accomplished using Eqs. (2–4). Known vaporization enthalpies of compounds with structural features and retention times similar to compound **1** were difficult to find in the

$$\begin{aligned} \Delta_1^g H_m(298 \text{ K}) (\text{kJ mol}^{-1}) = \Delta_1^g H_m(T_m \text{ K}) \\ + [10.58 + 0.26 C_p(l)] [T_m - 298.15 \text{ K}]/1000 \end{aligned} \quad (2)$$

$$\begin{aligned} \Delta_{cr}^g H_m(298 \text{ K}) (\text{kJ mol}^{-1}) = \Delta_{cr}^g H_m(T_m \text{ K}) \\ + [0.75 + 0.15 C_p(cr)] [T_m - 298.15 \text{ K}]/1000 \end{aligned} \quad (3)$$

Table 2 A Summary of the fusion enthalpies of compounds **1**, **2** ($M = 234.29$ g/mol), phenyl salicylate, and 4-hydroxyacetophenone

	m (mg)	Onset temperature (K)	$\Delta_{cr}^1 H_m$ (T_{fus} , kJ mol ⁻¹)	$C_p(l)/C_p(cr)$ ($J\ mol^{-1}\ K^{-1}$)	$\Delta_{cr}^1 H_m(298\ K)$ (kJ mol ⁻¹)
Compound 1	1.07	359.4	17.35		
	1.85	356.1	16.45		
		357.7	16.9 ± 1.3	410/282.5	12.5 ± 1.8
Compound 2	6.98	383.5	10.7		
	5.65	383.5	10.9		
	3.14	382.8	11.0		
Phenyl salicylate	10.13	312.9	10.9 ± 0.1	375/280.9	5.3 ± 1.7
	7.14	312.4			
	5.48	312.6			
4-Hydroxyacetophenone		312.7	18.4 ± 0.5	358.4 /246.8	16.5 ± 0.8
		383	18.0 ± 0.2 ^a	257.3/175.1	13.7 ± 1.4

^aReference [17].

$$\Delta_1^g H_m(298\ K) = \Delta_{cr}^g H_m(298\ K) - \Delta_{cr}^1 H_m(298\ K) \quad (4)$$

literature. Benzoin was the only compound with similar structural features and retention times close to compound **1** that could be identified. Although, the Antoine constants of liquid benzoin have previously been reported [15], the measurements were conducted at fairly high

temperatures, 404–616 K. The uncertainty of adjusting the vaporization enthalpy to $T = 298.15$ K was problematic. Consequently, benzoin was used as an unknown in mixture **1** of Table 6, and the resulting value was used as a standard in mixtures **2** and **3** also summarized in Table 6. The equations generated by correlating vaporization enthalpies

Table 3 Retention times (min) of a series hydroxy-ketones and esters related to compound **1**

	T (K)						
	454.1	459.3	464.2	469.1	474.1	479.1	484.1
Mixture 1							
CH ₂ Cl ₂	0.512	0.51	0.512	0.513	0.518	0.523	0.525
2-Hydroxyacetophenone	1.135	1.071	1.013	0.965	0.923	0.888	0.857
Methyl salicylate	1.213	1.139	1.072	1.016	0.967	0.927	0.891
4-Hydroxyacetophenone	2.213	1.995	1.807	1.653	1.519	1.41	1.313
Methyl 4-hydroxybenzoate	2.289	2.056	1.858	1.694	1.554	1.438	1.337
Phenyl salicylate	6.811	5.884	5.112	4.476	3.941	3.494	3.118
Benzoin	8.576	7.368	6.353	5.529	4.832	4.255	3.769
Compound 1	23.894	19.914	16.732	14.145	12.03	10.296	8.86
	T (K)						
	453.9	458.8	463.7	468.6	473.5	478.5	483.5
Mixture 2							
CH ₂ Cl ₂	0.516	0.52	0.518	0.521	0.52	0.52	0.529
2-Hydroxyacetophenone	1.128	1.07	1.013	0.965	0.923	0.884	0.858
Methyl salicylate	1.205	1.137	1.071	1.016	0.967	0.923	0.892
4-Hydroxyacetophenone	2.191	1.983	1.8	1.644	1.513	1.398	1.308
Methyl 4-hydroxybenzoate	2.27	2.047	1.852	1.688	1.549	1.428	1.332
Benzoin	8.493	7.301	6.304	5.48	4.792	4.213	3.735
Compound 1	23.795	19.873	16.694	14.099	11.971	10.233	8.797
	T (K)						
	454	459	463.8	468.9	473.8	478.7	454
Mixture 3							
CH ₂ Cl ₂	0.54	0.53	0.54	0.54	0.54	0.54	0.54
2-Hydroxyacetophenone	1.18	1.13	1.07	1.02	0.97	0.94	1.18
Ethyl salicylate	1.51	1.43	1.34	1.25	1.17	1.11	1.51
4-Hydroxyacetophenone	2.3	2.13	1.94	1.77	1.62	1.5	2.3
Benzoin	8.87	7.75	6.71	5.83	5.09	4.48	8.87
Compound 1	24.89	20.92	17.62	14.88	12.65	10.8	24.89

Table 4 Retention times (min) of a series of Ketones and Esters related to compound **2**

	T (K)					
	214.9	219.9	224.9	229.5	234.9	239.9
Mixture 4						
CH ₂ Cl ₂	1.879	1.899	1.911	1.929	1.945	1.96
2-Pentadecanone	3.543	3.32	3.186	3.041	2.929	2.835
7-Heptadecanone	4.916	4.471	4.162	3.876	3.642	3.456
Methyl palmitate	5.433	4.889	4.519	4.168	3.885	3.663
Methyl heptadecanoate	6.835	6.057	5.503	4.995	4.585	4.257
Methyl octadecanoate	8.8	7.672	6.851	214.9	5.527	5.055
Compound 2	9.189	8.14	7.354	6.645	6.053	5.572
Methyl nonadecanoate	11.536	9.902	8.695	7.65	6.795	6.121
	T(K)					
	483.8	488.8	498.7	503.8		
Mixture 5						
CH ₂ Cl ₂	1.578	1.62	1.675	1.722		
2-Pentadecanone	3.159	3.05	2.782	2.73		
7-Heptadecanone	4.499	4.209	3.636	3.474		
Methyl palmitate	5.013	4.65	3.941	3.735		
Methyl heptadecanoate	6.435	5.859	4.805	4.476		
Methyl octadecanoate	8.44	7.553	5.99	5.492		
Compound 2	8.681	7.9	6.438	5.969		
Methyl nonadecanoate	11.257	9.914	7.613	6.872		

Table 5 Literature vaporization enthalpies of standards

Compound	$\Delta_1^g H_m(T_m, K)$ (kJ mol ⁻¹)	T_m (K)	$C_p(l)(298 K)$ (J mol ⁻¹ K ⁻¹)	$\Delta_1^g H_m(298 K)$ (kJ mol ⁻¹)	References
2-Hydroxyacetophenone				59.6	[17]
METHYL salicylate				62.0	[15, 17, 18]
Ethyl salicylate	53.3	463	300.9	66.5	[18, 19]
Methyl 4-hydroxybenzoate				83.1	[17]
2-Pentadecanone	67.8	437	504.1	87.5	[15]
Methyl hexadecanoate				96.8	[20, 21]
Methyl heptadecanoate				100.8	[20, 21]
Methyl octadecanoate				105.9	[20, 21]
Methyl nonadecanoate				109.5	[20, 21]
4-Hydroxyacetophenone		335			
Phenyl salicylate		298			

^aReference [13]

with enthalpies of transfer from the condensed phase of the column to the vapor are provided beneath each correlation in Table 6, Eqs. (5–7). Similarly, for compound **2**, the results of duplicate correlations along with the equations generated, Eqs. (8) and (9), are likewise reported in Table 7. Uncertainties listed in Tables 6 and 7 were calculated from the uncertainties in slope and intercept of the correlation equations. All other uncertainties represent two standard deviations. It has previously been demonstrated that the use of esters as surrogate ketones as standards in these correlations is appropriate [16, 17].

$$\Delta_1^g H_m(298.15 K) \text{ (kJ mol}^{-1}\text{)}$$

$$= (2.412 \pm 0.225) \Delta_{\text{sln}}^g H_m(469 K) - (26.34 \pm 1.87) \\ r^2 = 0.987 \quad (5)$$

$$\Delta_1^g H_m(298.15 K) \text{ (kJ mol}^{-1}\text{)} \\ = (2.185 \pm 0.121) \Delta_{\text{sln}}^g H_m(469 K) - (22.81 \pm 1.79) \\ r^2 = 0.9909 \quad (6)$$

$$\Delta_1^g H_m(298.15 K) \text{ (kJ mol}^{-1}\text{)} \\ = (2.085 \pm 0.213) \Delta_{\text{sln}}^g H_m(466 K) - (15.21 \pm 3.05)$$

$$r^2 = 0.9795 \quad (7)$$

$$\begin{aligned} \Delta_f^{\circ} H_m(298.15 \text{ K}) \text{ (kJ mol}^{-1}\text{)} \\ = (1.31 \pm 0.001) \Delta_{\text{sln}}^{\circ} H_m(501 \text{ K}) - (17.50 \pm 0.712) \\ r^2 = 0.9948 \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta_f^{\circ} H_m(298.15 \text{ K}) \text{ (kJ mol}^{-1}\text{)} \\ = (1.246 \pm 0.045) \Delta_{\text{sln}}^{\circ} H_m(494 \text{ K}) - (28.62 \pm 0.62) \\ r^2 = 0.9960 \end{aligned} \quad (9)$$

Enthalpies of combustion

The substances investigated were available in only small amounts and this required the use of microcombustion techniques. The enthalpies of combustion were obtained using a two-cell Tian-Calvet-type microcalorimeter that has been described, previously [22–24]. The calorimeter has two measuring elements disposed symmetrically in a massive aluminum block. The block is fastened inside of a thermostated bath. The temperature of the water is maintained at $25 \pm 0.01^\circ\text{C}$. Around each calorimetric unit there are 60 copel-nicrothal thermocouples. The thermocouples were connected through a special switch, designed to prevent spurious thermoelectrical forces, to a Hewlett-Packard multimeter, model 34401A. The multimeter, in turn, was connected to a computer equipped with Benchlynk software, for acquisition of the experimental data. The areas of the ballistic curves were obtained by means of the Origin 50 program.

The micro-bombs built in the Laboratory of Thermodynamics of the Institute of Physical Chemistry of Bucharest have also been described elsewhere [23, 24]. The micro-bombs were manufactured as similarly as possible to eliminate distortions originating from heat transfer. The combustion micro-bomb is made of stainless steel and consists of three main parts: the top, the body, and the bottom. The components of the micro-bomb are shown in Fig. 2. The top of the bomb consists of a cylindrical component 19, surrounded by sleeve 5, provided with outside threads. The threads and a Viton rubber washer, 6, allow tightening and sealing of the top. Component 19 is penetrated by the metallic rods 7 lined by Teflon washers (not shown). These rods are extended at their bottoms, with stainless steel thick wire electrodes 9 and 18. The electrodes are connected by a platinum wire (0.05 mm diameter). Electrode 9 ends with a ring, which supports crucible 11. This is a disc made out of a platinum sheet (0.2 mm thickness). At the upper

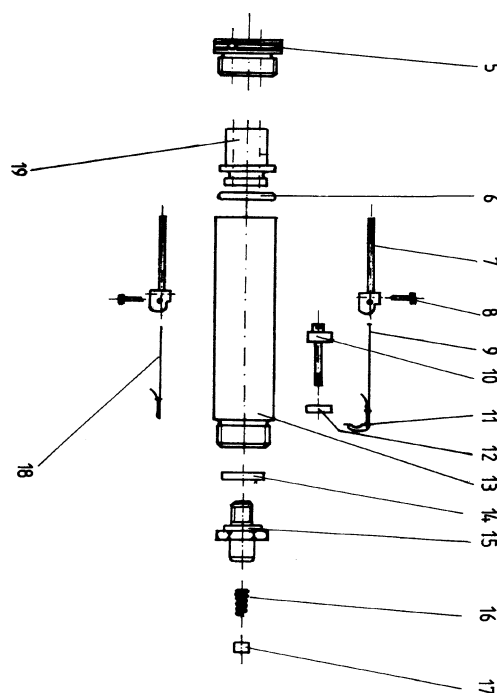


Fig. 2 Main components of the micro-bomb

Table 8 Enthalpies (kJ mol⁻¹) of combustion and formation of reference substances

Substance	$-\Delta_c H^\circ$	$-\Delta_f H^\circ$	$-\Delta_f H^\circ$ literature values
Salicylic acid	3014.8 ± 1.9	593.6 ± 2.1	592.1 ± 1.3 [25] 589.7 ± 1.1 [26]
Urea	635.6 ± 0.9	328.5 ± 1.0	333.1 ± 0.7 [27] 333.4 ± 0.2 [28]

end, outside the bomb, rods 7 are connected to the ignition device.

The body of the bomb is a cylinder (80 mm height, 14 mm inner diameter) provided with an inner thread at the upper part for attaching the top. At the lower part of the cylinder, there is a circular opening (5 mm diameter) destined to the insertion of the components of the third part of the bomb—the bottom.

The bottom of the micro-bomb is an ensemble of several small metallic components—10, 15, 17, inner Teflon washers, 12, and outer Viton rubber washers 14. This ensemble operates as a valve and is intended for the introduction of oxygen.

The samples were pressed in small discs of diameter 2.5 mm and height about 1 mm, so that the weight of the pellet did not exceed 8 mg. Ignition was triggered by means of a platinum wire stretched between the two electrodes on which a thin cotton thread 10 mm long ($\Delta_c h = -16.13 \text{ kJ g}^{-1}$) was knotted. The other end was placed in the crucible, below the pellet to be burned.

Table 6 Correlation of vaporization enthalpies with enthalpies of transfer for compound **1**

	Slope	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ (kJ mol ⁻¹)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298 \text{ K})^{\text{b}}$ (kJ mol ⁻¹ , literature)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298 \text{ K})$ (kJ mol ⁻¹ , calculated)
Mixture 1				
<i>o</i> -Hydroxyacetophenone	-4665.4	38.788	59.6 ^a	60.6
Methyl salicylate	-4815.7	40.037	62.0	63.4
4-Hydroxyacetophenone	-5668.9	47.131	82.5	79.3
Methyl 4-hydroxybenzoate	-5769.5	47.967	83.1	81.2
Phenyl salicylate	-6531.2	54.300	95.7	95.4
Benzoin	-6701.6	55.717		98.5 ± 12.9
Compound 1	-7580.3	63.022		114.9 ± 14.5
Mixture 2				
<i>o</i> -Hydroxyacetophenone	-4568.9	37.986	59.6	59.8
Methyl salicylate	-4722.0	39.259	62.0	62.7
4-Hydroxyacetophenone	-5671.3	471.51	82.5	80.8
Methyl 4-hydroxybenzoate	-5782.8	48.078	83.1	83.0
Benzoin	-6762.1	56.220	98.5	100.0
Compound 1	-7680.2	63.853		116.7 ± 7.9
Mixture 3				
<i>o</i> -Hydroxyacetophenone	-4330.7	36.005	59.6	59.9
Ethyl salicylate	-4829.7	40.154	66.5	68.5
4-Hydroxyacetophenone	-5447.5	45.291	82.8	79.2
Benzoin	-6634.3	55.158	98.5	99.8
Compound 1	-7611.2	63.280		116.7 ± 13.8

250 The completely equipped micro-bomb (filament, acces-
 251 sories, sample, 0.1 mL distilled water) was connected to the
 252 oxygen cylinder and then flushed with oxygen, keeping the
 253 top of the micro-bomb only partially closed. The top was then
 254 tightly closed and oxygen continued to flow until a 3040 kPa
 255 pressure was reached. The micro-bomb was disconnected

from the oxygen cylinder and introduced in the calorimetric
 cell.

The operations were repeated identically with the second
 micro-bomb, and both of them were connected to the ignition
 device.

The heat evolved is calculated as follows:

Table 7 Correlation of vaporization enthalpies with enthalpies of transfer for compound **2**

	Slope	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ (kJ mol ⁻¹)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298 \text{ K})^{\text{b}}$ (kJ mol ⁻¹ , literature)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298 \text{ K})^{\text{b}}$ (kJ mol ⁻¹ , calculated)
Mixture 4				
2-Pentadecanone	-6386.3	53.093	87.5	87.0
Compound 2	-7060.1	58.695		94.4 ± 1.8
7-Heptadecanone	-7075.0	58.818		94.5 ± 1.8
Methyl hexadecanoate	-7355.6	61.152	96.8	97.6
Methyl heptadecanoate	-7695.7	63.979	100.8	101.3
Methyl octadecanoate	-8059.4	67.002	105.9	105.2
Methyl nonadecanoate	-8436.5	70.138	109.5	109.3
Mixture 5				
2-Pentadecanone	-5645.3	46.93281	87.5	87.1
Compound 2	-6372.9	52.98179		94.6 ± 2.5
7-Heptadecanone	-6348.6	52.77977		94.4 ± 2.5
Methyl hexadecanoate	-6637.5	55.18157	96.8	97.4
Methyl heptadecanoate	-7022.0	58.37816	100.8	101.4
Methyl octadecanoate	-7404.3	61.55645	105.9	105.3
Methyl nonadecanoate	-7794.1	64.79709	109.5	109.4

$$Q = kA \quad (7)$$

where k denotes the calibration constant of the calorimeter and A the area delimited by the ballistic curve. The calibration constant of the calorimeter was determined by means of benzoic acid combustion (standard reference material from NIST) and calculated from the results of eight experiments. It was found to amount to 70.31 ± 0.22 and 70.64 ± 0.22 J/unit area for the two micro-bombs.

The calorimeter was tested for combustion in micro-bombs with two reference materials: salicylic acid and urea [25–28]. Combustion data from at least eight runs yielded the values of enthalpies of combustion and formation, shown in Table 8, which are fairly comparable to the values from the literature. From these experiments, we concluded that our equipment was capable of measuring thermal effects as low as 50 J with accuracy higher than 0.1%.

The results of the combustion experiments on compounds **1** and **2** are shown in Tables 9 and 10, respectively. At least 10 runs were done for each compound, but some of them were rejected because of some doubt about combustion completeness. In runs used in data calculation, there was no evidence of soot formation in the bomb.

All reported errors follow the recommendations for assignment of uncertainties from reference [29].

Results and discussion

The structure of the enolic portion of compound **1** is very similar to the measured structure of benzoylacetone which has been studied both by X-ray and neutron diffraction [30]. Both structural motifs are found to be essentially planar. The X-ray and neutron diffraction data of benzoylacetone suggests a large π delocalization with the hydrogen lying in a very flat asymmetric single minimum potential. As might be expected, the bond angles and rigid nature of bicyclic compound **3** renders its structure more like an enolic ketone rather than like benzoylacetone **4**. Table 11 and Fig. 3 summarize some of the structural similarities observed for the enol portion of the three molecules. Most bond distances and bond angles in compounds **1** and **4** are within experimental error

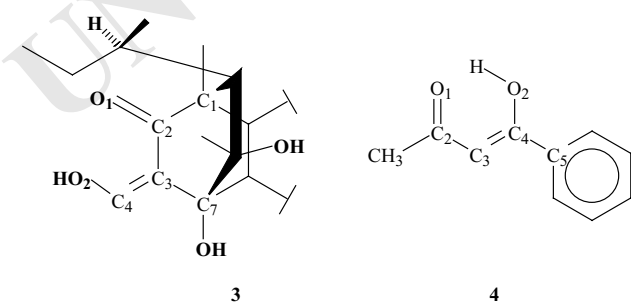


Fig. 3 Numbering in compound **3** and in benzoylacetone (**4**)

Table 9 Combustion data for compound **1**^a

m_p (mg)	q_b (J)	A	Q_p (J)	$\Delta_c u_{\text{cor}}^0$ (J g ⁻¹)
4.68	7.41	2.313	155.18	33072
3.92	13.14	2.040	130.54	33139
2.40	2.43	1.165	79.87	33025
2.98	29.04	1.810	98.78	33048
4.71	19.08	2.476	155.77	32986
2.79	17.70	1.557	92.26	32974

^aMean value, $\Delta_c u_{\text{cor}}^0 = -33041$ J g⁻¹; standard deviation, ± 61 J g⁻¹; standard error of the mean, ± 25 J g⁻¹; m_p , sample mass; q_b , heat due to ignition; Q_p , heat of burning of the sample; $\Delta_c u_{\text{cor}}^0$, corrected (Washburn) specific energy of combustion.

Table 10 Combustion data for compound **2**

m_p (mg)	q_b (J)	A	Q_p (J)	$\Delta_c u_{\text{cor}}^0$ (J g ⁻¹)
2.77	9.04	1.540	99.20	35720
5.57	5.48	2.930	200.87	35900
2.66	11.76	1.530	95.77	35911
3.56	11.92	1.974	127.49	35716
2.30	36.78	1.702	82.84	35898
2.69	9.50	1.500	96.44	35755

Note. Mean value, $\Delta_c u_{\text{cor}}^0 = -35817$ J g⁻¹; standard deviation, ± 95 J g⁻¹; standard error of the mean, ± 39 J g⁻¹; for key, see Table 8 footnote

of each other. The only exception is the comparison of the bond distance between C(4) bond O(2) in benzoylacetone (**4**) and C(16) bond O(2) in compound **1** which compares the difference between a conjugated phenyl group versus a hydrogen. Unlike benzoylacetone, in which the phenyl group is completely planar with the enol, the torsion angle between the enol and the conjugated phenyl ring in compound **1** is 41.6° , suggesting significant loss of conjugation.

Condensed phase standard molar enthalpies of combustion and formation of the two ketones are summarized in Tables 9, 10, and 12. Values of -285.83 and -393.51 kJ mol⁻¹ were used for the enthalpy of formation of H₂O(l) and CO₂(g) [31]. The standard molar enthalpies of sublimation of these two materials were obtained by combining the vaporization and fusion enthalpies adjusted to 298.15 K [32]. The results are summarized in Table 13. Sublimation enthalpies of 128.6 ± 2.8 and 99.8 ± 2.8 kJ mol⁻¹ were evaluated for compounds **1** and **2**, respectively. The vaporization enthalpies of compounds **1** and **2** can also be estimated by a number of group methods. We have chosen to use the following simple equation to do so [33]:

$$\Delta_1^{\text{g}} H_{\text{m}}(298 \text{ K}) (\text{kJ mol}^{-1}) = 4.69(n_{\text{C}} - n_{\text{Q}}) + 1.3n_{\text{Q}} + 3.0 + \sum n_i F_i b_i + C \quad (10)$$

where n_{C} and n_{Q} refer to the number of carbon and quaternary carbon atoms, respectively, and n_i , F_i , and b_i refer to the

Table 11 Some bond distances and angles measured for compounds **4**, **1**, and **3**^a

	Compound 4	Compound 1	Compound 3
Bond distance (Å)			
O(1)–O(2), O(1)–O(2), O(1)–O(2)	2.502(4)	2.501	2.656
O(1)–C(1), O(1)–C(1), O(1)–C(1)	1.286(4)	1.293(2)	1.227
O(2)–C(4) O(2)–C(16) O(2)–C(4)	1.293(4)	1.274(2)	1.333
C(2)–C(3), C(1)–C(2), C(2)–C(3)	1.414(4)	1.407(2)	1.477
C(3)–C(4), C(2)–C(3), C(3)–C(4)	1.405(4)	1.399(2)	1.331
CH ₃ –C(2), C(1)–C(15), C(1)–C(2)	1.499(4)	1.494(2)	1.516
Bond angle (°)			
O(1)–C(2)–C(3), O(1)–C(1)–C(2), O(1)–C(2)–C(3)	122.1(3)	121.9(15)	121.6
C(2)–C(3)–C(4), C(1)–C(2)–C(16), C(2)–C(3)–C(4)	119.7(2)	117.7(15)	122.5
C(3)–C(4)–O(2), C(2)–C(16)–O(2), C(3)–C(4)–O(2)	120.9(3)	124.9(16)	124.12

^aSee Fig. 3.**Table 12** Standard enthalpies (kJ mol⁻¹) of combustion and formation of compounds **1** and **2** at $T = 298.15$ K in the crystalline phase

Compound	$-\Delta_c H^\circ$	$-\Delta_f H^\circ(\text{s})$	$-\Delta_f H^\circ(\text{s,calc})$
1	7812.1 ± 14.3	199.1 ± 16.4	–
2	8398.8 ± 22.3	79.7 ± 22.9	69.1

of the aromatic rings (8 C_B–(H) (110.45), 2 C_B–(C_B) (41.5), C_B–(C) (23.1), C_B–(C_d) 23.8 kJ mol⁻¹), a methylene group (CH₂–(CO)(C_B) 22.6 kJ mol⁻¹), and ring strain for a 1,3-cycloheptadiene (27.6 kJ mol⁻¹). This amounts to a total of –89 kJ mol⁻¹, which is quite comparable to an experimental value of -70.5 ± 20.5 kJ mol⁻¹, given the approximations involved and the non-planarity of the two aromatic rings with each other and with the exocyclic hydroxymethylene group (Fig. 1).

Similar treatment of compound **2** is somewhat more problematic. Estimation of strainless 2:3,6:7-dibenzobicyclo[3.2.2]nona-2,6-dien-4-one by the Benson method results in an estimated gas phase enthalpy of formation of 9.5 kJ mol⁻¹. This compares to the experimental value of 20.1 ± 23.1 kJ mol⁻¹. Molecular mechanics calculations of the bicyclo[3.2.2]nonane ring system suggests a strain energy of approximately 64 kJ mol⁻¹ [35].

Liquid phase enthalpies of atomization of both compounds have also been estimated by means of the Allen–Skinner scheme, with parameter values (including bond energies and bond interactions, specific to keto–enol tautomers) recommended by Vilcu and Perisanu [36, 37]. In this case, strain energies were not considered.

By examining the differences between experimental and estimated enthalpies of formation and atomization of compounds **1** and **2** listed in Table 14, a considerable stabilization through the annelation of two benzenoid rings to the cycloheptane ring is not observed for both of these compounds, as in the case of most dibenzocycloalkane compounds investigated previously [1–3].

In the case of compound **1**, the geometry imposes non-coplanarity of the two benzenoid rings, thus diminishing their conjugation. A similar difference of 39 kJ mol⁻¹ is observed between experimental and calculated enthalpies of

number of functional groups (n), the effect of hybridization and substitution of the carbon bearing the function group on the functional group contribution (F), and the contribution of each functional group (b) summed over all the functional groups present in the molecule. For compounds with only one functional group such as compound **2**, all F values are equal to 1.0. The C term corrects for branching near the functional group (-2.0 kJ mol⁻¹), the effect of incorporating various functional groups in a ring (2.9 kJ mol⁻¹) and for intramolecular hydrogen bonding in β diketones (-18 kJ mol⁻¹). Most of these effects are small, with the exception of intramolecular hydrogen bonding. Estimation of the vaporization enthalpy for compound **1** results in a value of $[16 \times 4.69 + 3 + (1.08 + 0.85)/2 \times 10.5 + 29.4 \times 0.69 - 18] = 93.2$ kJ mol⁻¹, which is somewhat less than the 116.1 ± 12.1 kJ mol⁻¹ evaluated in this work. Results for compound **2**, a much simpler system $[17 \times 4.69 + 3.0 + 10.5 - 2.0 + 2.9] = 94.1$ kJ mol⁻¹, is in excellent agreement with the value determined in the work 94.5 ± 2.2 kJ mol⁻¹.

Gas phase enthalpy of formation of compound **1** can also be estimated. Using the recently revised gas phase enthalpy of formation of the enol form of acetylacetone, -378.2 kJ mol⁻¹ [17] and Benson group values [34], the enthalpy of formation of compound **1** can be approximated by removing the two methyl groups from Z -4-hydroxy-3-penten-2-one ($+85.35$ kJ mol⁻¹), adding the contributions

Table 13 Standard enthalpies (kJ mol⁻¹) of formation of compounds **1** and **2** at $T = 298.15$ in the gas phase

Compound	$\Delta_f H^\circ(\text{s})$	$\Delta_f^\circ H_m(298\text{ K})$	$\Delta_{\text{cr}}^\circ H_m(298\text{ K})$	$\Delta_f H^\circ(\text{g})(298\text{ K})$
1	-199.1 ± 16.4	116.1 ± 12.1	12.5 ± 1.8	-70.5 ± 20.5
2	-79.7 ± 22.9	94.5 ± 2.2	5.3 ± 1.7	20.1 ± 23.1

Table 14 Enthalpies (kJ mol⁻¹) of atomization of compounds **1** and **2** in the liquid state

Compound	$\Delta_{\text{at}}H^{\circ}(\text{exp})$	$\Delta_{\text{at}}H^{\circ}(\text{calc})$ aldo-enol	$\Delta_{\text{at}}H^{\circ}(\text{calc})$ (di)carbonyl	$\Delta_{\text{at}}H^{\circ}(\text{calc})$ keto-enol
1	14753.0	14795.3	14774.9	14798.9
2	15537.7		15561.3	

atomization of 5,7-dihydro-6*H*-dibenzo[*a,c*]cyclohepten-6-one, in the liquid state, if combustion data from reference [1] and heat of fusion from reference [38] are used. In this molecule, steric hindrance between the two ortho hydrogens imposes non-coplanarity as well. Enolization of compound **1**, followed by closing of a six-membered ring through a hydrogen bond, does not introduce the expected stability, especially in the case of the keto-enolic structure, which is more sterically destabilized than the aldo-enol probably because of the endocyclic double bond. Widely divergent estimates have been reported for planar biphenyl depending on method. Values as high as 19 kJ mol⁻¹ [37] 12.5 kJ mol⁻¹ [39], 8.4 kJ mol⁻¹ [40], 6.0 kJ mol⁻¹ [41], and 4.7 kJ mol⁻¹ [42] are in the literature.

Ketone **2** is destabilized by about 25 kJ mol⁻¹. The strain introduced by the bicyclic moiety of approximately 64 kJ mol⁻¹ [36] also compensates the stabilization due to the dibenzo-annelation.

Acknowledgments We acknowledge the funding from the National Science Foundation (MRI award #0420497) and from the Missouri Research Board for the purchase of the APEX II diffractometer and Oxford LT device.

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