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The enthalpies of formation of two dibenzocyclooctadienones

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Abstract

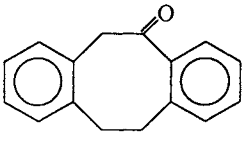
The standard molar enthalpies of formation ($\Delta_f H_m^0(s)/kJ\,mol^{-1}$) for 2,3:6,7-dibenzocycloocta-2,6-dien-1-one and 2,3:7,8-dibenzocycloocta-2,7-dien-1-one [6*H*-11,12-dihydro-dibenzo[*a*,*e*]cycloocten-5-one (ketone **1**) and 10*H*-11,12-dihydrodibenzo[*a*,*d*]-cycloocten-5-one (ketone **2**), respectively] were derived from enthalpies of combustion, measured by means of a microbomb calorimeter. The fusion and vaporization enthalpies of these compounds were obtained from DSC and correlation gas chromatography measurements. The standard molar enthalpies of formation in the gas phase were calculated by combining the condensed phase standard molar enthalpies of formation with the fusion and vaporization enthalpies adjusted to 298.15 K. Values for $\Delta_f H_m^0(g)$ of (-39.9 ± 5.5) and (-14.8 ± 5.3) kJ mol^{-1} were obtained for 2,3:6,7-dibenzocycloocta-2,6-dien-1-one and 2,3:7,8-dibenzocycloocta-2,7-dien-1-one, respectively. Quantum chemical calculations are reported for the compounds investigated experimentally and an additional four isomers. Isomerization enthalpies are derived from computed energies. The enthalpies of formation are also calculated by group additivity, compared with the experimental values and then correlated with the structure of the molecules investigated. The X-ray analysis of ketone **1** is also reported.

Keywords: Dibenzocyclooctadienones; DSC; Enthalpies of combustion; Fusion; Vaporization; Formation; Ab initio calculations

1. Introduction

This paper continues the thermochemical investigation of some dibenzoannelated cycloalkane derivatives. In previous papers, the standard enthalpies of formation of some dibenzocycloheptane ketones [1] and of some dibenzocycloheptane alcohols [2] were measured.

With the aim of a comparative study of the enthalpies of formation of dibenzocycloalkane derivatives, data on the standard molar enthalpies of formation of the two dibenzocyclooctadienones, ketones **1** and **2** are added in this paper:



2,3:6,7-dibenzocycloocta-2,6-dien-1-one (ketone **1**)

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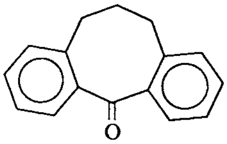
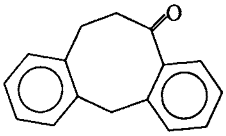
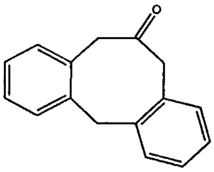


2,3:7,8-dibenzocycloocta-2,7-dien-1-one (ketone **2**)

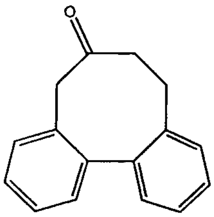


2,3:5,6-dibenzocycloocta-2,5-dien-1-one (ketone **3**)

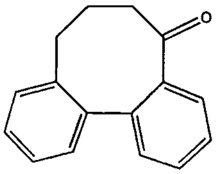
During the course of our investigations of the thermal properties of ketones **1** and **2**, some concern was expressed regarding the structure of ketone **1**. A question arose regarding whether the structure reported as ketone **1** was actually ketone **3**. The ^{1}H and ^{13}C NMR spectra of **1** were not particularly revealing. The formation of ketone **1** requires two ring expansions and the possibility of other rearrangements competing with ring expansion could not be conclusively eliminated. As a result, the structure of ketone **1** was unambiguously determined by X-ray crystallography. This paper reports the structure of ketone **1** and thermochemical properties of ketones **1** and **2**. These results are compared to ab initio quantum mechanical calculations for ketones **1**–**3** as well as for three additional isomers, ketones **4**–**6**.



3,4:6,7-dibenzocycloocta-3,6-dien-1-one (ketone **4**)



3,4:5,6-Dibenzocycloocta-3,5-dien-1-one (ketone **5**)



2,3:4,5-Dibenzocycloocta-2,4-dien-1-one (ketone **6**)

2. Experimental

2.1. Synthesis and purification

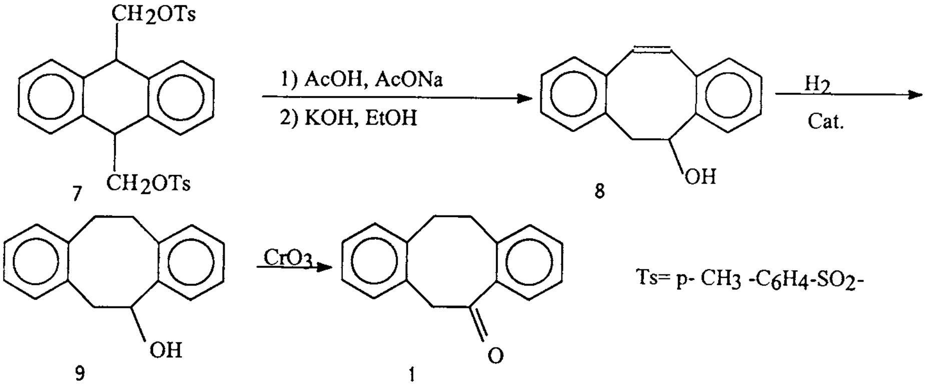
Ketone **1** was obtained using procedures described in previous papers [3,4]. The buffered acetolysis of ditosylate **7** afforded the alcohol **8** in high yield. Catalytic hydrogenation of **8** gave rise to the saturated alcohol **9**, which was subsequently oxidized to ketone **1** (Scheme 1).

The synthesis of ketone **2** was performed using a reaction sequence described in the literature [5] (Scheme 2).

The spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS) of ketones **1** (mp = 368 K, after two recrystallizations from ethanol) and **2** (mp = 421 K, after two recrystallizations from 2-propanol) have previously been reported [5,6]. Samples analyzed by gas chromatography to be over 99.9% pure were used in the subsequent studies.

2.2. X-ray crystal structure

Colorless crystals of ketone **1** were grown by slow evaporation from ethanol solution at ambient temperature. A crystal with dimensions 0.34 mm × 0.16 mm × 0.10 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection was performed using a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) equipped with a sealed tube X-ray source at 170 K. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.4° in ϖ) scans. The data set collected consisted of 3636 frames with a frame width of 0.3° in ϖ and counting time of 15 s/frame at a crystal to detector distance of 4.900 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix

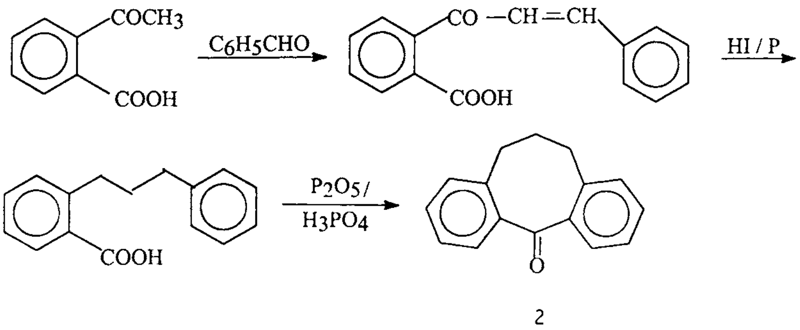


Scheme 1.

determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 2001) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *xyz* centroids of 4048 reflections ($\theta < 28.3^\circ$). Collected data were corrected for systematic errors using SADABS [7] based on the Laue symmetry using equivalent reflections. The integration process yielded 11,712 reflections of which 1592 were independent reflections.

Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement were carried out using the SHELXTL software package (Sheldrick, G.M., Bruker Analytical X-ray Division, Madison, WI, 2001). The structure was solved by Direct methods and refined successfully in the space group *C*2/*c*. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_O^2 - F_C^2)^2$. 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 $R(F) = 4.5\%$ for 1176 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 11.6\%$; $s = 1.0$ for all data. The carbonyl O is disordered due to forced crystallographic symmetry. The O atom was refined with a 50% occupancy factor. Structure refinement parameters are listed in Table 1. A projection view of ketone **1** with non-hydrogen atoms represented by 50% probability ellipsoids, and showing the atom labeling is presented in Fig. 1.

Complete listings of the atomic coordinates for the non-hydrogen atoms and the geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are deposited



Scheme 2.

Table 1
Crystal data and structure refinements for ketone **1**

Identification code	CCDC#181758
Empirical formula	$C_{16}H_{14}O$
Formula weight	222.27
Temperature (K)	170 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions (Å)	$a = 18.2308$, $\alpha = 90°$ $b = 5.10800$ (10), $\beta = 117.934$ (1)° $c = 14.0319$ (3), $\gamma = 90°$
Volume (Å^3, *z*)	1154.45 (4), 4
Density (Mg/m^3)	1.279
Absorption coefficient (mm^{-1})	0.078
F(0 0 0)	472
Crystal size (mm)	0.34 × 0.16 × 0.10
θ range for data collection	2.53–28.27°
Limiting indices	$-24 \leq h \leq 21$, $-6 \leq k \leq 6$, $-18 \leq l \leq 18$
Reflections collected	11712
Independent reflections	1436 ($R_{int} = 0.038$)
Completeness to $\theta = 28.27°$	100.0%
Absorption correction	None
Maximum and minimum transmission	0.9922 and 0.9740
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	1436/0/79
Goodness of fit on *F*	1.051
Final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0449$, $wR2 = 0.1083$
R indices (all data)	$R1 = 0.0567$, $wR2 = 0.1156$
Largest diff. peak and hole (eA^{-3})	0.177 and −0.177

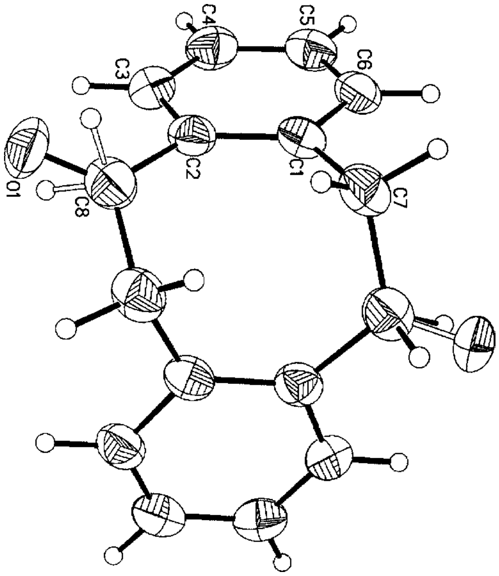


Fig. 1. A projection view of ketone **1** illustrating the forced crystallographic symmetry.

with the Cambridge Crystallographic Data Center (CCDC#181758).

2.3. Fusion enthalpies

Fusion enthalpies were measured on a Perkin Elmer DSC 7 using sealed stainless steel cells. The instrument was calibrated using indium metal. Temperature was scanned at 2 K/min. The results are reported in Table 2. No other transitions were observed between room temperature and the melting temperature.

2.4. Vaporization enthalpies

The vaporization enthalpies were derived by correlation gas chromatography (CGC) using a Hewlett Packard GC 5890 Series II. The column used for all experiments was a HP1 (cross linked methyl silicone gum) with the dimensions 12 m × 0.2 mm × 0.32 μm (film thickness). A total of four mixtures have been measured. All mixtures were prepared by dissolving the respective compounds in methylene chloride. The first mixture contained the reference compounds: benzophenone, 9-heptadecanone and heptadecanoic acid

Table 2
Experimental fusion enthalpies by DSC

Compound	*m* (g)	T_{fus} (K)	$\Delta_{fus}H_m(T_{fus})$ (kJ mol^{-1})
Ketone **1**			
Run 1	0.00236	366.3	17.40
Run 2	0.00161	364.1	17.62
Run 3	0.00192	366.2	16.84
Run 4	0.00199	368.6	16.70
Run 5	0.00218	367.9	17.52
Mean value		366.6	17.2 ± 0.5
Ketone **2**			
Experiment 1	0.00486	420.1	28.03
Experiment 2	0.00506	420.1	27.12
Experiment 3	0.00413	419.7	28.28
Mean value		420.0	27.8 ± 0.7

Table 3
Some thermochemical properties of the vaporization standards

	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}(T_{\mathrm{m}}(\mathrm{K}))$	T_{m} (K)	C_{Pm}(l) (298.15 K) ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) ($\mathrm{kJ\,mol^{-1}}$) [8]
Benzophenone	65.1	448	300.1	78.4
9-Heptadecanone	78.3	454	568.0	103.0
Methyl tetradecanoate	75.6	404	515.8	90.9
Methyl heptadecanoate	84.4	436	611.5	107.8
Methyl octadecanoate	83.2	442	643.4	108.8

methyl ester and the two ketones. The second mixture contained the same reference compounds but only ketone **1**. The third mixture contained the two ketones and two more reference compounds, methyl tetradecanoate and methyl octadecanoate. Ketone **1** exhibited lower retention times than ketone **2**. The fourth mixture was run as a control to demonstrate that the vaporization enthalpies of the classes of compounds used as standards correlate with each other. Vaporization enthalpy data and estimated molar heat capacities of the standards are detailed in Table 3 [8]. Eq. (1) was used to adjust vaporization enthalpies from the literature when necessary to 298.15 K:

$$\begin{aligned}\Delta_{\mathrm{vap}}H_{\mathrm{m}}&(298.15\,\mathrm{K/J\,mol^{-1}})\\ &= \Delta_{\mathrm{vap}}H_{\mathrm{m}}(T_{\mathrm{m}})\\ &\quad+[10.58+0.26(C_{\mathrm{Pm}}(\mathrm{l})(298.15\,\mathrm{K})]\\ &\quad\times[T_{\mathrm{m}}-298.15]\end{aligned} \tag{1}$$

The terms T_{m} and C_{Pm}(l)(298.15 K) represent the mean temperature of measurement and the heat capacity of the compounds at 298.15 K. The latter was estimated by group additivity [9,10].

The experimental retention time data of methylene chloride and the different compounds in each mixture and the temperatures of each experiment are shown in Table 4. The corrected retention times were calculated by subtracting the retention time of the methylene chloride from the retention times of each compound at each temperature. Methylene chloride is not retained by the column under these conditions. Note that the retention time of CH_2Cl_2 increases with increasing temperature, contrary to the retention times of the other components. The increase in the retention time of CH_2C1_2 with temperature is a consequence of the corresponding increase in the viscosity of the He carrier gas.

2.5. Enthalpies of combustion

The substances investigated were available in small amounts and required the use of microcombustion techniques. The enthalpies of combustion were obtained using a two cell Tian–Calvet type microcalorimeter that has been previously described [11]. The calorimeter has two measuring elements disposed symmetrically in a massive aluminium block. The block is fastened inside of a thermostated bath. The temperature of the water is maintained at 298.15 ± 0.01 K. All 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 for acquisition of the experimental data. The maximum deviation (in mV) of the ballistic curves, which is proportional to the areas that these delimitate, was obtained by means of the Benchlynk program.

The microbombs constructed in the Laboratory of Thermodynamics of the Institute of Physical Chemistry of Bucharest have also been described [12]. They have been designed to burn samples that weigh less than 8 mg. The microbombs were manufactured as similarly as possible, to eliminate distortions originating from thermal transfer. The samples were pressed into small discs 2.5 mm in diameter and about 1 mm in height so that the mass of the sample did not exceed 8 mg. Ignition was carried out using cotton thread, 10 mm long, knotted on platinum wire and stretched between the two electrodes. The heat of combustion of the cotton thread was measured as −16399 ± 23 J/g. The contribution of the cotton thread is listed as q_c, the heat due to ignition in Table 5. Both the sample and reference cell were flushed and filled with oxygen to a final pressure of 3040 kPa. Both cells were inserted

Table 4
Gas chromatographic retention times t_r (min)

	T (K)						
	414.65	419.55	424.55	429.55	434.45	439.25	444.15
Mixture 1							
CH_2Cl_2	0.215	0.220	0.219	0.219	0.222	0.222	0.226
Benzophenone	2.895	2.447	2.079	1.791	1.554	1.355	1.195
9-Heptadecanone	10.607	8.290	6.643	5.385	4.405	3.630	3.020
Methyl heptadecanoate	22.192	17.197	13.420	10.600	8.448	6.795	5.510
Ketone **1**	10.607	8.610	7.010	5.785	4.815	4.040	3.417
Ketone **2**	14.490	11.694	9.482	7.775	6.425	5.350	4.487
	414.65	419.55	424.55	429.55	434.45	439.35	444.05
Mixture 2							
CH_2Cl_2	0.219	0.219	0.221	0.224	0.227	0.225	0.232
Benzophenone	2.912	2.457	2.091	1.799	1.558	1.362	1.197
9-Heptadecanone	10.515	8.318	6.673	5.412	4.420	3.648	3.030
Methyl heptadecanoate	22.225	17.231	13.471	10.645	8.469	6.819	5.521
Ketone **1**	10.515	8.553	7.010	5.797	4.822	4.050	3.415
	414.9	419.7	424.6	429.6	434.5	439.1	444.3
Mixture 3							
CH_2Cl_2	0.222	0.220	0.224	0.225	0.221	0.225	0.229
Benzophenone	2.915	2.457	2.093	1.799	1.553	1.355	1.198
Methyl tetradecanoate	5.279	4.266	3.493	2.893	2.409	2.028	1.731
9-Heptadecanone	10.556	8.323	6.681	5.415	4.413	3.630	3.034
Methyl heptadecanoate	22.283	17.262	13.502	10.659	8.481	6.795	5.531
Ketone **1**	10.556	8.578	7.030	5.820	4.835	4.035	3.424
Ketone **2**	14.510	11.700	9.525	7.819	6.448	5.355	4.503
Methyl octadecanoate	36.060	27.576	21.294	16.590	13.021	10.290	8.266
	414.9	419.7	424.6	429.6	434.4	439.2	444.1
Mixture 4							
CH_2Cl_2	0.215	0.219	0.223	0.225	0.221	0.223	0.223
Benzophenone	2.902	2.452	2.091	1.796	1.554	1.352	1.188
2-Pentadecanone	4.54	3.717	3.07	2.56	2.15	1.818	1.555
Methyl tetradecanoate	5.238	4.256	3.489	2.887	2.408	2.022	1.718
2-Heptadecanone	11.832	9.372	7.493	6.036	4.911	4.014	3.319
Methyl hexadecanoate	13.683	10.771	8.548	6.844	5.53	4.49	3.689
Methyl heptadecanoate	22.16	17.195	13.449	10.611	8.449	6.766	5.479

into the calorimeter, initially at 298.15 ± 0.01 K and connected to the ignition device. Only the sample microbomb contained the cotton thread.

Ketone **2** did not compress well into pellets; consequently, paraffin film was used to seal the crucible. The enthalpy of combustion of the paraffin film was measured separately and was found to be 46,230 ± 19 kJ g^{-1}. Ignition was triggered after introduction of the microbombs in the calorimetric block and a stable base line was established. A ballistic type curve was recorded following ignition,

$$Q = kV \qquad (2)$$

where k stands for the calibration constant of the calorimeter (J mV^{-1}) and V for the maximum deviation (mV). The calibration constant of the calorimeter was determined by means of benzoic acid combustion (standard reference material from NIST) and was calculated from the results of eight experiments. It was found to amount to 879.46 ± 0.90 J mV^{-1}.

Table 5
Combustion data of ketone **1**[a]

m (g)	V (mV)	q_c (J)	m_{par} (g)	q_{par} (J)	Q (J)	Δu_{exp} (J/g)	Δu_{cor} (J/g)
0.00391	0.258	4.88	0.00170	79.13	227.27	36641	36637
0.00475	0.660	6.18	0.00474	219.8	580.12	36628	36625
0.00410	0.336	6.83	0.00299	138.82	195.80	36623	36620
0.00469	0.673	3.25	0.00899	416.45	591.57	36646	36642
0.00445	0.303	4.72	0.00215	99.96	266.63	36642	36638
0.00373	0.262	7.81	0.0018	85.74	229.91	36632	36628
0.00366	0.220	4.88	0.00118	54.81	193.81	36644	36640
0.00326	0.249	6.83	0.00380	92.90	219.34	36695	36691
0.00620	0.419	7.48	0.00288	133.74	368.63	36683	36679
0.00657	0.398	5.52	0.00222	103.19	349.91	36711	36707

[a] Average value $\Delta u_{cor} = -(36.651 \pm 0.019)\,\mathrm{kJ\,g^{-1}}$; (8146.4 ± 4.3) $\mathrm{kJ\,mol^{-1}}$ (uncertainty ±2 standard deviations of the mean); m: sample mass; q_c: heat due to ignition; m_{par}: mass of the paraffin film; q_{par}: heat of burning of the paraffin film; Q: total heat; Δu_{exp}: experimental specific energy of combustion; Δu_{cor}: corrected (Washburn) specific energy of combustion.

Table 6
Combustion data of ketone **2**[a]

m (g)	V (mV)	Q (J)	q_c (J)	Δu_{exp} ($\mathrm{J\,g^{-1}}$)	Δu_{corr} ($\mathrm{J\,g^{-1}}$)
0.00622	0.260	228.38	4.55	36730	36726
0.00360	0.154	134.92	2.76	36703	36699
0.00704	0.310	265.33	6.98	36722	36718
0.00498	0.214	188.30	5.68	36699	36695
0.00641	0.276	242.44	6.98	36764	36760
0.00572	0.245	215.01	5.36	36739	36736
0.00603	0.257	225.92	4.62	36716	36712
0.00650	0.277	243.49	5.05	36694	36690

[a] Average value (-36.721 ± 0.017) $\mathrm{kJ\,g^{-1}}$; (8161.9 ± 3.7) $\mathrm{kJ\,mol^{-1}}$; For a key, see footnote in Table 5.

The results of the combustion experiments are shown in Tables 5 and 6. At least 10 runs were made for each compound, but some of them were rejected because of incomplete combustion. The data in the tables come from experiments that gave reproducible results with no evidence of soot present following combustion. The reliability of the calorimeter was confirmed by means of combustion of other reference compounds such as salicyclic acid and urea [12]. All uncertainties reported below are two standard deviations unless otherwise noted.

3. Results

Condensed phase standard molar enthalpies of combustion and formation of the two ketones are summarized in Table 7. Values of −285.83 and $-393.51\,\mathrm{kJ\,mol^{-1}}$ were used for the enthalpy of formation of $H_2O(l)$ and $CO_2(g)$ [13]. The standard molar enthalpies of sublimation of these two materials were obtained by combining the vaporization and fusion enthalpies adjusted to 298.15 K [14].

3.1. Vaporization enthalpies

Enthalpies of transfer from solution to the vapor, $\Delta_{sln}^{g}H_m(T_m)$, were measured by correlation gas chromatography. They 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 $1/T$ ($\mathrm{K^{-1}}$) as previously reported [14]. The temperature T_m refers to the mean temperature of measurement. Correlating $\Delta_{sln}^{g}H_m(T_m)$ with the vaporization enthalpies of the standards at 298.15 K, results in a linear relationship that can be used to obtain $\Delta_{vap}H_m$ (298.15 K) of the unknowns. The enthalpies of transfer measured for the standards and for ketones **1** and **2** are summarized in Table 8. The correlation equations used to

Table 7
Standard enthalpies of combustion and formation of crystalline ketones **1** and **2** at 298.15 K

Compound	$-\Delta_c H^0$ ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta_f H^0(s)$ ($\mathrm{kJ\,mol^{-1}}$)
Ketone **1**	8153.8 ± 4.3	143.2 ± 4.3
Ketone **2**	8169.4 ± 3.7	127.6 ± 3.7

Table 8

A summary of the vaporization enthalpies obtained by correlation gas chromatography for mixtures 1–4 and the corresponding correlation equations

Compound	$\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}})$ (kJ mol^{-1})	$\Delta_{\mathrm{vap}} H_{\mathrm{m}}$ (298.15 K) literature (kJ mol^{-1})	$\Delta_{\mathrm{vap}} H_{\mathrm{m}}$ (298.15 K) calculated (kJ mol^{-1})
Mixture 1			
Benzophenone	52.66	78.4	79.1
9-Heptadecanone	67.75	103.0	100.7
Methyl heptadecanoate	73.86	107.8	109.4
Ketone **1**	61.23		91.3
Ketone **2**	62.68		93.4
$\Delta_{\mathrm{vap}} H_{\mathrm{m}}(298.15\,\mathrm{K}) = (1.43 \pm 0.19)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}}) + (3.64 \pm 2.9)$;		$r^2 = 0.983$	
Mixture 2			
Benzophenone	53.09	78.39	79.3
9-Heptadecanone	67.43	102.99	100.2
Methyl heptadecanoate	73.93	107.8	109.7
Ketone **1**	60.83		90.6
$\Delta_{\mathrm{vap}} H_{\mathrm{m}}(298.15\,\mathrm{K}) = (1.46 \pm 0.23)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}}) + (1.74 \pm 3)$;		$r^2 = 0.975$	
Mixture 3			
Benzophenone	53.40	78.4	78.1
9-Heptadecanone	68.04	95.5	97.0
Methyl heptadecanoate	74.53	107.8	105.3
Methyl tetradecanoate	63.36	90.9	90.9
Methyl octadecanoate	78.16	108.8	110.0
Ketone **1**	61.35		88.4
Ketone **2**	63.05		90.5
$\Delta_{\mathrm{vap}} H_{\mathrm{m}}(298.15\,\mathrm{K}) = (1.29 \pm 0.092)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}}) + (9.43 \pm 1.8)$;		$r^2 = 0.985$	
Mixture 4			
Benzophenone	53.62	78.4	76.2
2-Pentadecanone	61.70	83.7	87.4
Methyl tetradecanoate	63.50	90.9	89.9
2-Heptadecanone	69.28	95.8	98
Methyl hexadecanoate	71.12	101.3	100.5
Methyl heptadecanoate	74.90	107.8	105.8
$\Delta_{\mathrm{vap}} H_{\mathrm{m}}(298.15\,\mathrm{K}) = (1.39 \pm 0.16)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}}) + (1.55 \pm 2.69)$;		$r^2 = 0.952$	

calculate the vaporization enthalpies are included in the table for each mixture. The equation of each line was generated by a linear regression analysis. Fig. 2 illustrates the correlation observed for mixture 3. As noted above, the results from mixture 4 suggest that the enthalpies of transfer of the compounds chosen as standards correlate with each other.

3.2. Fusion enthalpy

The fusion enthalpy of ketones **1** and **2**, $\Delta_{\mathrm{fus}} H_{\mathrm{m}}(T_{\mathrm{fus}})$, was adjusted from T_{fus} to 298.15 K using the following equation [14,15].

$$\begin{aligned}\Delta_{\mathrm{fus}} H_{\mathrm{m}}&(298.15\,\mathrm{K}/\mathrm{J\,mol^{-1}})\\ &= \Delta_{\mathrm{fus}} H_{\mathrm{m}}(T_{\mathrm{fus}}) + [0.75 + 0.15(C_{\mathrm{Pm}}(\mathrm{s})(298.15\,\mathrm{K})]\\ &\quad \times [T_{\mathrm{fus}} - 298.15] - [10.58\\ &\quad + 0.26(C_{\mathrm{Pm}}(\mathrm{l})(298.15\,\mathrm{K})](T_{\mathrm{fus}} - 298.15) \qquad (3)\end{aligned}$$

The terms $C_{\mathrm{Pm}}(\mathrm{s})$ (298.15 K) and $C_{\mathrm{Pm}}(\mathrm{l})$ (298.15 K) refer to the molar heat capacities of the solid and liquid state, respectively, of each ketone estimated at 298.15 K by group additivity [9]. The results are

Table 9
A summary of the fusion, vaporization and sublimation enthalpies of ketones **1** and **2**

Compound	C_{Pm}(l) ($J\,mol^{-1}$)	C_{Pm}(s) ($J\,mol^{-1}$)	$\Delta_{fus}H_m(T_{fus})$ ($kJ\,mol^{-1}$)	T_{fus} (K)	$\Delta_{fus}H_m$ (298.15 K) ($kJ\,mol^{-1}$)	$\Delta_{vap}H_m$ (298.15 K) ($kJ\,mol^{-1}$)	$\Delta_{sub}H_m$ (298.15 K) ($kJ\,mol^{-1}$)
Ketone **1**	364.8	275.8	17.2 ± 0.5	366.6	12.8 ± 1.8	90.6 ± 2.0	103.3 ± 3.2
Ketone **2**	364.8	275.8	27.8 ± 0.7	420	20.1 ± 2.9	92.0 ± 2.9	112.8 ± 4.1

reported in Table 9 and will discussed below. Uncertainties represent two standard deviations of the mean. The uncertainty associated with this term was arbitrarily assigned as a fraction (0.167) of the total temperature adjustment.

3.3. Sublimation enthalpy

The sublimation enthalpies of ketones **1** and **2** are summarized in Table 9. The difference in the sublimation enthalpies of the two ketones is mainly due to the difference in fusion enthalpy.

3.4. Enthalpies of formation

The standard enthalpies of formation in the solid and ideal gas states were calculated using the data in Tables 9 and 10. In Table 10, experimental values of these quantities are shown together with values estimated by means of the Benson group additivity method. The values reported by the Benson method are for strainless molecules, i.e. ring-corrections were ignored. The parameters needed for the estimation were taken from the literature [16].[1] Also included in Table 10 are estimations of molar enthalpies of formation of ketones **3**–**6**.

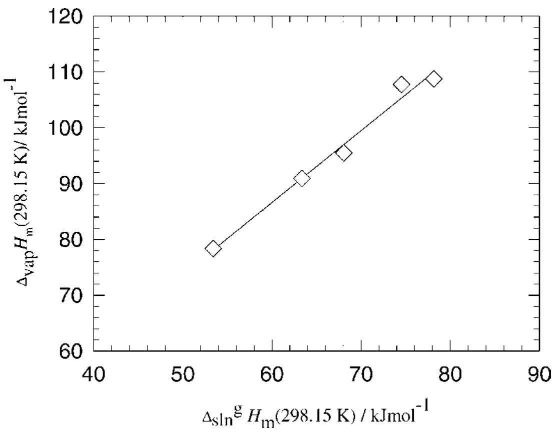


Fig. 2. A plot of $\Delta_{vap}H_m$ (298.15 K) against $\Delta^{g}_{sln}H_m(T_m)$ for mixture 3.

3.5. Quantum chemical calculations

Ab initio quantum chemical calculations [2] were carried out for geometry optimized structures of ketone isomers **1**–**4** at the RHF/3-21G(d)//RHF/3-21G(d) level [17].[3] Numerical vibrational frequencies at 298.15 K and unscaled zero-point energies were also computed at same calculational level to obtain thermally corrected total energies. The individual energy contributions (including 0–298 K rotational and translational corrections) and the final total energy calculations are depicted in Table 11. For completeness, calculational results on the two remaining isomeric (uniquely “biphenyloid”) dibenzocyclooctadienones—ketones **5** and **6**—are also included in Table 11.

4. Discussion

It may be concluded, by examining the differences between experimental and estimated enthalpies of formation of ketones **1** and **2** listed in Table 10, that both these ketones are stabilized by roughly

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[1] Group values were taken from reference [16]; a group value of −19.2 kJ mol^{-1} for C–(H)$_2$(C$_B$)$_2$ was derived from the Benson group values [16] and the gas phase molar enthalpy of formation of diphenylmethane ($-\Delta_f H^0$(g): 165 ± 1.5 kJ mol^{-1}) [20].

[2] More precisely, we used the SPARTAN SGI Version 5.0.3 Open GL built under IRIX 6.2 by Wavefunction Inc., Irvine, CA, 1997 program for our quantum chemical calculations.

[3] For a more thorough description of our calculational level, see [17].

Table 10
Standard molar enthalpies of sublimation and formation of ketones **1** and **2** in the gas phase at 298.15 K; comparisons with estimations by group additivity

Compound	$\Delta_f H^0$(s) (kJ mol^{-1})	$\Delta_{sub}H_m$ (kJ mol^{-1})	$\Delta_f H^0$(g) (kJ mol^{-1})	$\Delta_f H^0$(g) (kJ mol^{-1}) Benson[a]
Ketone **1**	−143.2 ± 4.3	103.3 ± 3.2	−39.9 ± 5.5	2.6
Ketone **2**	−127.6 ± 3.7	112.8 ± 4.1	−14.8 ± 5.3	18.3
Ketone **3**				4.5
Ketone **4**				6.9
Ketone **5**				2.0
Ketone **6**				−1.5

[a] Calculated from Benson group values [16] ignoring ring strain and using a group value of −19.2 kJ mol^{-1} for C–(H)$_2$(C$_B$)$_2$ [20].

30–40 kJ mol^{-1} through the annelation of two benzenoid rings to the cyclooctane ring. The quantum chemical computations of Table 11 also confirm the stability order of ketones **1** and **2** obtained experimentally. The calculated difference ($\Delta\Delta_f H$) of 10 kJ mol^{-1} is in relatively good agreement with the experimental difference of 24.1 ± 10.8 kJ mol^{-1}. This gives us confidence in our theoretical predictions for the other isomeric dibenzocyclooctadienones. With the exceptions of ketones **1** and **3**, the ab initio results shown in Table 11 are also in good relative agreement with the empirical estimations obtained by group additivity.

The additional stabilization observed here relative to those estimated by group methods, agree with previous results reported for dibenzoannelated cycloheptane derivatives [1,2]. For example, considering the seven membered ring homologue of ketone **2**, dibenzosuberone (2,3:6,7-dibenzocyclohepta-2,6-dien-1-one), a value of about 35 kJ mol^{-1} has been reported for the additional stabilization of this compound, due to the attachment of two benzenoid rings to the saturated carbocycle. A value exceeding 30 kJ mol^{-1} was reported by Verevkin [18] for anthrone with its central six-membered ring.

Examination of the relative energies calculated by ab initio methods for the dibenzocyclooctadienones in Table 11 reveals that ketone **4** is stabilized anywhere from ∼12 to 24 kJ mol^{-1} compared to isomeric ketones **1** and **2**, even though the carbonyl groups in ketones **1** and **2** are conjugated to benzene rings. The strain energy associated with a sufficient flattening of the ring necessary for conjugation may be large enough that the ring remains non-planar at the cost of conjugation. Loss of conjugation of the carbonyl with the benzene ring can increase the ground state

Table 11
RHF/3-21G(d)//RHF/3-21G(d) energies of isomeric dibenzocyclooctadienones; a comparison of ab initio results with those estimated by group additivity

Compound	E_{total} (hartree)[a]	ZPE (kJ mol^{-1})[b]	Therm. corr. (kJ mol^{-1})[c]	E_{298} (hartree)[d]	$\Delta_f H_{rel}$ (kJ mol^{-1})[e] ab initio	$\Delta\Delta_f H^{rel}_{(g)}$ (kJ mol^{-1})[e] Benson[f]
Ketone **1**	−685.07083	726.4	757.7	−684.78223	31.2	4.1
Ketone **2**	−685.06697	726.0	757.6	−684.77842	41.2	19.8
Ketone **3**	−685.07324	727.6	758.3	−684.78441	25.5	6.0
Ketone **4**	−685.07562	726.2	756.9	−684.78733	17.8	8.4
Ketone **5**[g]	−685.07676	724.3	753.9	−684.78961	11.8	3.5
Ketone **6**	−685.08311	728.3	758.7	−684.79412	(0.0)	(0.0)

[a] Total energies.
[b] Zero-point energies.
[c] Thermal corrections for translational, rotational, and vibrational enthalpy changes from 0 to 298 K.
[d] Thermally corrected total energies, where $E_{298} = E_{Total}$ + therm. corr. and 1 Hartree = 2625.5 kJ mol^{-1}.
[e] Calculated relative heats of formation, where (0.0) refers, by definition, to the lowest energy species.
[f] Reference [16].
[g] One imaginary frequency of 53.85i cm^{-1} was ignored.

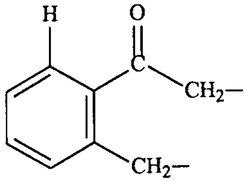
Table 12
Bond lengths (Å) measured for ketone **1**[a]

Bond	Å
C(1)–C(6)	1.3967(16)
C(1)–C(7)	1.5125(17)
C(2)–C(8)	1.5134(15)
C(4)–C(5)	1.3803(19)
C(7)–C(8)#1	1.5275(17)
C(8)–C(7)#1	1.5275(17)
C(1)–C(2)	1.4010(17)
C(2)–C(3)	1.3928(17)
C(3)–C(4)	1.3832(18)
C(5)–C(6)	1.3803(18)
C(8)–O(1)	1.0875

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

energy of the molecule because of the inductive effect of the non-conjugated phenyl ring on the electron deficient carbonyl carbon. Given similar losses in conjugation, this destabilizing effect would be expected to be greater in ketone **2** than in ketone **1**. The experimental data appears to bear this out. Ketone **1** is more stable than ketone **2**.

When this qualitative explanation is subjected to the other available experimental evidence, the data appears to be inconclusive. An examination of the crystal structure of ketone **1** reveals a dihedral angle of 28.3° between the carbonyl group and carbons C2–C3 of the benzene ring. To the extent that the solid state models the gas phase structure, conjugation should be attenuated by this angle. The bond length of the carbonyl group is not reliable because of disorder due to forced crystallographic symmetry (see Fig. 1, Table 12). An examination of the bond lengths between C(2)–C(8) (and crystallographically equivalent C(2)#1–C(8)#1 (see Table 12)) and C(1)–C(7) reveals identical distances between the four atoms. This distance between the benzene ring and the carbonyl group is an average of C(2)–C(8) and C(2)#1–C(8)#1. Nevertheless, the uncertainty associated with this bond length is very similar to the others in the crystal structure, suggesting both C(2)–C(8) and C(2)#1–C(8)#1 bond lengths to be very similar. An examination of crystal structures of 14 other *ortho* substituted conjugated aromatic ketones in the Cambridge Database with the following structure motif resulted in an average bond distance of (1.498 ± 0.03) Å ($\pm 2\sigma$).



This compares to a value of (1.5134 ± 0.03) Å found in ketone **1**. Conjugation between the ring and the carbonyl group in the solid state of **1** on the basis of this argument would be expected to be attenuated. In contrast, the infrared frequency of 1681 $\mathrm{cm^{-1}}$ (KBr) exhibited by ketone **1** in the solid state when compared to the frequency observed in acyclic 1,6-diphenylhexane-1,6-dione ($\nu_{\max}$ 1681 $\mathrm{cm^{-1}}$ (Nujol) [19]), appears normal for a ketone conjugated to a phenyl group. The infrared frequency for ketone **2** (1633 $\mathrm{cm^{-1}}$ (CCl_4)), can be compared to the frequency observed in 4-phenylbenzophenone (1648 $\mathrm{cm^{-1}}$ (Nujol) [19]). The crystal structure of ketone **2** is not available; thus any correlation of bond length with infrared frequency must await further experimental structural or gas phase studies.

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