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Thermochemistry of aromatic ketones. Experimental enthalpies of formation and structural effects[1]

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Abstract

The standard enthalpies of formation $\Delta_f H^o$ (liq. or cr.) at the temperature $T = 298.15$ K were measured using combustion calorimetry for benzophenone (**A**), 1-indanone (**B**), α-tetralone (**C**), 9-fluorenone (**D**), anthrone (**E**) and dibenzosuberone (**F**). The standard enthalpies of vaporization $\Delta_v H^o$ or sublimation $\Delta_s H^o$ of A-F and 5,7-dihydro-6H-dibenzo[a,c]cyclohepten-6-one (**G**) were obtained from the temperature function of the vapor pressure measured in a flow system. Enthalpies of fusion $\Delta_m H$ of solid compounds were measured by DSC. From the enthalpies of formation of the gaseous compounds of **A–G** the values of their strain enthalpies were derived and structural effects discussed.

		$\Delta_f H^o$ (liq. or cr.) kJ mol^{-1}	$\Delta_v H^o$ or $\Delta_s H^o$ kJ mol^{-1}	$\Delta_m H^o$ kJ mol^{-1}	$\Delta_f H^o$(g) kJ mol^{-1}
A	cr.	-42.21 ± 0.96	93.1 ± 2.2	—	50.9 ± 2.4
B	cr.	-145.25 ± 0.87	83.51 ± 0.73	17.78	-61.7 ± 1.1
C	liq.	-160.55 ± 0.71	65.28 ± 0.30	—	-95.27 ± 0.77
D	cr.	-7.71 ± 0.71	93.9 ± 1.6	14.85	86.2 ± 1.8
E	cr.	-85.0 ± 1.2	106.10 ± 0.81	—	21.1 ± 1.5
F	cr.	-48.8 ± 1.1	109.3 ± 1.5	17.15	60.5 ± 1.9
G	cr.	—	95.61 ± 0.78	18.16	58.4 ± 14.0

Keywords: Enthalpy of formation; Enthalpy of sublimation; Enthalpy of vaporization; Ketone

1. Introduction

The body of thermochemical data for ketones is considerable [1]. In a previous paper [2] we investigated the germinal interactions in diketones and

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refined the values of additivity group increments (Benson scheme [3,4]) with our own and those available from the literature. The lack of information concerning aromatic compounds has been detected by the review of the thermochemical properties of ketones. In order to understand the interrelations of structure and energetics of aromatic cyclic ketones, the values of the standard enthalpies of formation $\Delta_f H^o(g)$ of mono- and di-phenyl substituted cyclic ketones were measured. The resulting quantities of conjugation of one or two phenyl substituents with the double bond of the carbonyl group in five-membered rings (1-indanone and 9-fluorenone), six-membered rings (α-tetralone and anthrone) and seven-membered rings (dibenzosuberone and 5,7-dihydro-6H-dibenzo[a,c]cyclohepten-6-one) were derived with the help of the group additivity values. The thermochemical quantities of benzophenone were remeasured here in order to get an accurate comparison of conjugation in the acyclic ketones.

2. Experimental

The samples of benzophenone (**A**), 1-indanone (**B**), α-tetralone (**C**), 9-fluorenone (**D**), anthrone (**E**) and dibenzosuberone (**F**) were commercially available from Aldrich, Acros and Merck. The pure sample of 5,7-dihydro-6H-dibenzo[a,c]cyclohepten-6-one (**G**) was donated by Dr. Stefan Perisanu (Universitatea 'Politehnica' Bucuresti, Romania). The solid samples having a mass fraction purity about 0.99, were purified by repeated recrystallization from ethanol and petroleum ether and further sublimated in vacuum directly before combustion in order to avoid any traces of the solvent. The liquid compound α-tetralone (**C**) was purified by repeated distillation under reduced pressure. To avoid the traces of water in samples for the combustion experiments, the purified liquid samples were dried over molecular sieves and distilled once more before the combustion. Such a procedure provided colourless material, and the absence of water was shown by Karl Fischer titration. The determination of purity (see Table 1) was carried out by GC ($\geq 0.01\%$) and DSC measurements of the melting process [5].

All compounds were handled under an inert atmosphere (N_2) using carefully dried solvents. We used the following equipment – GC: Carlo Erba Fraktometer Vega Series GC 6000, Hewlett Packard Integrator 3390A, N_2-Flow 2 ml/min., SE-30 capillary column 25 m. Standard temperature program: 313 K for 5 min. with 0.167 K s^{-1} up to 523 K. DSC: Perkin–Elmer DSC-2C with Olivetti PC M 28.

For the measurements of the enthalpies of combustion of **A** to **F** an isoperibolic macrocalorimeter with a stirred water bath was used. The substances were filled in polyethylene ampoules or pressed into tablets of

Table 1
Purity, temperature of fusion, density $\rho_{(293\ K)}$, specific heat $c_{p(298.15\ K)}$ and expansion coefficient of the materials

	Purity GC	in % DSC	T_{fus} [a] K	$\rho_{(293\ K)}$ [b] g cm^{-3}	$c_{p(298.15\ K)}$ [a] J K^{-1} g^{-1}	10^{-6} $(\delta V_m/\delta T)_p$ [c] dm^3 K^{-1}
A	99.99	—	—	1.19	1.80	0.1
B	99.99	99.99	312.9	1.25	1.30	0.1
C	99.88	—	—	1.10	1.59	1.0
D	99.99	99.98	353.3	1.27	1.38	0.1
E	99.99	—	—	1.33	1.55	0.1
F	99.99	99.98	305.5	1.31	1.72	0.1
G	99.99	99.98	350.3	—	—	0.1
oil [d]		—	—	0.880	0.84	1.0
cotton [e]		—	—	1.500	1.67	0.1
polyethylene [f]		—	—	0.920	2.53	0.1

[a] From DSC measurements; the usual error bars of $\Delta_m H^o$ measurements ±0.21 kJ mol^{-1}.

[b] Measured with pycnometer.

[c] Estimated.

[d] $CH_{1.940}$, $\Delta_c u^o(\text{oil}) = -46003.6 \pm 4.0$ J g^{-1}.

[e] $CH_{1.774}$ $O_{0.887}$, $\Delta_c u^o(\text{cotton}) = -16945.2 \pm 4.2$ J g^{-1}.

[f] $CH_{1.930}$, $\Delta_c u^o(\text{polyethylene}) = -46361.0 \pm 3.1$ J g^{-1}.

Table 2
Results from measurements of the vapor pressure p with transpiration method

	T [a] K	m [b] mg	V_{N2} [c] dm^3	p [d] mbar	$\Delta_v H^o_T$ or $\Delta_s H^o_T$ kJ mol^{-1} [e]
	298.6	8.53E − 01	132.6	8.749E − 04	
	303.7	7.23E − 01	53.93	1.822E − 03	
A	308.8	9.92E − 01	43.94	3.069E − 03	92.4 ± 2.2
	313.6	1.43E + 00	36.82	5.286E − 03	(sublimation)
	317.7	1.81E + 00	27.53	8.949E − 03	
	319.9	1.50E + 00	19.39	1.051E − 02	
	288.4	1.53E + 00	29.95	9.566E − 03	
	293.4	1.54E + 00	16.79	1.715E − 02	
B	298.3	4.81E + 00	29.52	3.053E − 02	83.51 ± 0.73
	303.2	2.21E + 00	7.76	5.348E − 02	(sublimation)
	308.1	2.05E + 00	4.38	8.756E − 02	
	318.4	4.14E + 00	3.37	2.304E − 01	
	323.1	3.52E + 00	2.09	3.157E − 01	
	328.2	4.28E + 00	1.75	4.582E − 01	
B	333.4	4.46E + 00	1.29	6.483E − 01	60.33 ± 0.42
	338.3	4.51E + 00	0.97	8.710E − 01	(vaporization)
	343.4	3.82E + 00	0.600	1.192E + 00	
	348.3	3.68E + 00	0.420	1.642E + 00	
	283.5	9.79E − 01	27.62	6.066E − 03	
	288.5	1.68E + 00	29.47	9.735E − 03	
C	294.5	9.64E − 01	9.90	1.656E − 02	
	298.7	3.59E + 00	25.57	2.382E − 02	
	308.4	1.56E + 00	4.75	5.577E − 02	64.96 ± 0.30
	313.4	1.67E + 00	3.33	8.503E − 02	
	318.3	1.73E + 00	2.41	1.218E − 01	
	323.5	1.65E + 00	1.54	1.812E − 01	
	323.7	1.10E + 00	40.93	3.717E − 03	
	328.8	1.48E + 00	34.53	5.918E − 03	
D	333.9	1.71E + 00	23.38	1.008E − 02	91.6 ± 1.6
	338.9	9.91E − 01	7.74	1.760E − 02	(sublimation)
	343.6	1.53E + 00	8.14	2.584E − 02	
	348.7	1.36E + 00	4.51	4.146E − 02	
	333.4	8.59E − 01	270.8	4.072E − 04	
	338.4	7.67E − 01	132.9	7.384E − 04	
	343.6	1.63E + 00	170.1	1.224E − 03	
E	348.7	1.13E + 00	69.50	2.071E − 03	102.96 ± 0.81
	353.9	1.04E + 00	37.67	3.537E − 03	(sublimation)
	358.5	1.60E + 00	38.11	5.372E − 03	
	363.6	1.87E + 00	25.55	9.318E − 03	
	367.6	9.55E − 01	9.32	1.307E − 02	
	314.1	2.53E − 01	95.30	3.355E − 04	
	318.6	3.23E − 01	74.95	5.419E − 04	
	323.4	3.27E − 01	41.17	9.953E − 04	
F	328.4	5.04E − 01	37.25	1.696E − 03	90.0 ± 1.5
	333.3	7.00E − 01	30.05	2.914E − 03	(vaporization)
	338.4	1.27E + 00	37.50	4.232E − 03	

Table 2
(Continued)

	T [a] K	m [b] mg	V_{N2} [c] dm^3	p [d] mbar	$\Delta_v H_T^o$ or $\Delta_s H_T^o$ kJ mol^{-1} [e]
	343.2	1.22E+00	24.06	6.355E − 03	
	324.4	8.54E − 01	91.02	1.176E − 03	
	329.5	9.99E − 01	71.35	1.754E − 03	
	348.2	6.80E − 01	8.10	1.049E − 02	
	353.2	6.64E − 01	5.29	1.569E − 02	
	322.9	6.03E − 01	78.20	9.184E − 04	
	328.2	9.95E − 01	73.81	1.604E − 03	
G	333.2	1.11E + 00	50.32	2.617E − 03	93.40 ± 0.78
	338.2	1.51E + 00	40.92	4.389E − 03	(sublimation)
	343.2	1.67E + 00	27.08	7.320E − 03	
	347.2	1.13E + 00	12.99	1.034E − 02	

[a] Temperature of saturation, N_2 gas stream 0.95–1.88 dm^3 h^{-1}.
[b] Mass of transferred sample cooled down by temperature of condensation $T_{cond} = 243$ K.
[c] Volume of nitrogen used to transfer mass of sample m.
[d] Vapor pressure at temperatures T of experiment, corrections for residual vapor pressure at T_{cond}.were made.
[e] Measured values at average of temperature range of experiment.

mass ~500 mg, which were burned in oxygen at a pressure 30.45 bar with a volume of 0.78 cm^3 of water added to the bomb. The completeness of combustion of the crystalline samples was insured by the addition about 50 mg of oil on the tablet. The detailed procedure has been described previously [6]. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (sample SRM 39i, National Bureau of Standards). From six experiments was measured $\varepsilon_{calor} = 25112.6 \pm 1.9$ J K^{-1} (0.0077%). For the reduction of the data to standard conditions conventional procedures were used [7]. The atomic weights used were those recommended by the IUPAC commission [8]. The density of solid compounds was determined by submerging a tablet of the substance in a calibrated 10 cm^3 pycnometer containing water. The density of the liquid α-teralone was taken from the Acros catalog. The specific heat capacities were measured with the DSC. The summary of auxiliary quantities for the combustion experiments is given in Table 1.

The enthalpies of sublimation of compounds **A**–**B** and **D**–**G** and enthalpy of vaporization of compound **C** were determined with the method of transference in a saturated N_2-stream [6,9,10]. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (±0.1 K), a nitrogen stream (1–2 cm^3 h^{-1}) was passed through the U-tube and the transported amount of material was condensed in a cooled at T_{cond} trap. The amount of condensed product was determined by GC analysis using an internal standard. The vapor pressure at the saturation temperature and the molar enthalpy of vaporization or sublimation were calculated from the linear correlation of the logarithm of the amount of transported compound against T^{-1}. From the slope of this correlation $\Delta_s H^o = -R[\mathrm{d}\ln(m/V_{N2}/\mathrm{d}T^{-1}]$ (with R = ideal gas constant, m = amount of transported compound, V_{N2} = volume of transportation gas, T = temperature) the observed enthalpy of vaporization $\Delta_v H_T^o$ or sublimation $\Delta_s H_T^o$ at the temperature T was obtained (see Table 2).

3. Results and discussion

This paper reports the thermochemical measurements (combustion calorimetry, transpiration method and DSC) leading to the standard enthalpies of formation $\Delta_f H^o$ (g) of aromatic ketones at the temperature $T = 298.15$ K.

Results for a typical combustion experiment on each compound are given in Table 3. The individual values of $-\Delta_c u^o$, together with the mean and its

Table 3
Results from typical combustion experiments at 298.15 K [a]

	A	**B**	**C**	**D**	**E**	**F**
m (substance)/g [b]	0.425755	0.353146	0.606265	0.460164	0.503654	0.594761
$m'_{\text{(cotton)}}$/g [b]	0.000880	0.000945	0.001015	0.001083	0.000917	0.000933
$m''_{\text{(oil)}}$/g [b]	0.052918	0.052997	—	0.069367	0.065242	0.068621
$m'''_{\text{(polyethylene)}}$/g	—	—	0.269255	—	—	—
ΔT_c/K [c]	0.70201	0.58043	1.35656	0.76315	0.82751	0.98652
$\varepsilon_{\text{calor}}(-\Delta T_c)$/J	−17629.35	−14576.21	−34066.73	−19164.61	−20780.91	−24774.12
$\varepsilon_{\text{cont}}(-\Delta T_c)$/J	−9.15	−7.38	−18.82	−9.85	−10.80	−13.11
$\Delta E_{\text{corr.}}$/J [d]	10.05	7.86	17.32	11.72	12.46	14.59
$-m'\Delta_c u'$/J	14.90	16.01	17.19	18.35	15.53	15.80
$-m''\Delta_c u''$/J	2434.42	2438.06	—	3191.14	3001.38	3156.83
$-m'''\Delta_c u'''$/J	—	—	12482.92	—	—	—
$\Delta_c u$ (substance)/J g^{-1}	−35648.8	−34320.7	−35573.0	−34665.5	−35264.1	−36314.6
$\Delta_c H^o$ (substance)/kJ mol^{-1}	−6501.03	−4539.66	−5205.39	−6250.72	−6854.48	−7569.17
$\Delta_f H^o$ (substance)/kJ mol^{-1}	−43.74	−145.24	−158.85	−8.22	−83.80	−48.45

[a] For the definition of the symbols see Ref. [7], macrocalorimeter: $T_h = 298.15$ K; $V_{\text{bomb}} = 0.2664$ l; $p^i_{\text{gas}} = 30.45$ bar; $m^i_{\text{water}} = 0.78$ g; $E_{\text{ignition.}} = 1.5$ J; $m_{\text{platin}} = 12.18$ g.
[b] Corrected masses obtained from weight by calculating the buoyancy.
[c] $\Delta T_c = T^f - T^i + \Delta T_{\text{corr.}}$, $\varepsilon_{\text{calor}} = 25112.6 \pm 1.9$ J K^{-1} (0.0077%); $\varepsilon_{\text{cont}}(-\Delta T_c) = \varepsilon^i_{\text{cont}}(T_i - 298\text{ K}) + \varepsilon^f_{\text{cont}}(298\text{ K} - T_f + \Delta T_{\text{corr.}})$.
[d] ΔE_{corr}. is sum of items 81–85, 87–90, 93 and 94 in Ref. [7].

Table 4
Values of specific energies of combustion $(-\Delta_c u^o)$ at $T = 298.15$ K as the results of all combustion experiments for aromatic ketones

A	**B**	**C**	**D**	**E**	**F**
$-\Delta_c u^o$:/J g^{-1}					
35648.8	34320.7	35573.0	34665.5	35249.7	36304.5
35653.2	34335.9	35556.6	34665.9	35270.4	36303.0
35657.3	34313.0	35558.8	34665.1	35265.5	36314.6
35669.6	34313.1	35557.0	34676.9	35239.7	36313.9
				35264.1	36329.0
Mean value:					
35657.2	34320.7	35561.4	34668.4	35257.9	36313.0
±4.5	±5.4	±3.9	±2.9	±5.7	±4.7

Table 5
Experimental results for aromatic ketones **A-G** at 298.15 K (kJ mol^{-1})

	State	$-\Delta_c H^o$ (cond.) [a]	$\Delta_f H^o$ (cond.)	$\Delta_s H^o$ [b]	$\Delta_m H^o$	$\Delta_f H^o$ (g)	H_s [f]
A	cr.	6502.56 ± 0.96	−42.21±0.96	93.1±2.2	—	50.9±2.4	+7.4
B	cr.	4569.66 ± 0.87	−145.25±0.87	83.51±0.73	17.78	−61.7±1.1	+15.2
C	liq.	5203.70 ± 0.71	−160.55±0.71	65.28±0.30 [c]	—	−95.27±0.77	+4.1
D	cr.	6251.23 ± 0.71	−7.71±0.71	93.9±1.6	14.85	86.2±1.8	+23.5
E	cr.	6853.3 ± 1.2	−85.0±1.2	106.10±0.81	—	21.1±1.5	−19.7
F	cr.	7568.8 ± 1.1	−48.8±1.1	92.1±1.5 [c]	17.15	60.5±1.9 [d]	+40.7
G	cr.	—	−37.2±14.0 [e]	95.61±0.78	18.16	58.4±14.0	+32.1

[a] Taken from the specific enthalpies of combustion in Table 4.
[b] From the measurements of vapor pressures at different temperatures from Table 2 using the Clausius–Clapeyron equation.
[c] Enthalpy of vaporization.
[d] By the estimation of $\Delta_f H^o$ (g) the enthalpy of sublimation was calculated as sum of $\Delta_v H^o + \Delta_m H^o$.
[e] The result was taken from Ref. [17].
[f] For the definition see the text.

standard deviation, are given in Table 4. To derive $\Delta_f H_m^o$ from $\Delta_c H_m^o$ the following molar enthalpies of formation were used [8]: for $H_2O(l)$: -285.83 ± 0.04, for $CO_2(g)$: -393.51 ± 0.13 kJ mol^{-1}. Table 5 lists the derived standard molar enthalpies of combustion and of the formation in the condensed and a gaseous states. The given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials.

The resulting enthalpies of sublimation $\Delta_s H^o$ or vaporization $\Delta_v H^o$ at 298.15 K are recorded in Table 5. Since the temperature range of vapor pressure measurements was usually above 298.15 K the derived values of enthalpies of vaporization or sublimation had to be corrected to this standard temperature. The values of corrections were estimated with the help of the 'Sidgwick correction':

$$\Delta_s H^o(T_{\text{average}}) - \Delta_s H_m^o(298.15\,\text{K}) = -0.06 \cdot (T_{\text{average}} - 298.15),$$

following the recommendation of Chickos et al. [11]. The values of the estimated corrections to the enthalpy of sublimation were: benzophenone (**A**) [$T_{\text{average}} =$ 309.2 K, 0.66 kJ mol^{-1}]; 1-indanone (**B**) [$T_{\text{average}} =$ 298.2 K, 0.00 kJ mol^{-1}]; 9-fluorenone (**D**) [$T_{\text{average}} =$ 336.2 K, 2.30 kJ mol^{-1}]; anthrone (**E**) [$T_{\text{average}} =$ 350.5 K, 3.14 kJ mol^{-1}]; [$T_{\text{average}} = 355.0$ K, 3.41 kJ mol^{-1}]; 5,7-dihydro-6H-dibenzo[a,c]cyclohepten-6-one (**G**) [$T_{\text{average}} = 335.0$ K, 2.21 kJ mol^{-1}]. In the same manner corrections were made for the enthalpies of vaporization of α-tetralone (**C**) [$T_{\text{average}} = 303.4$ K, 0.32 kJ mol^{-1}, 1-indanone (**B**) [$T_{\text{average}} = 333.3$ K, 2.10 kJ mol^{-1}], and dibenzosuberone (**F**) [$T_{\text{average}} = 333.6$ K, 2.13 kJ mol^{-1}]. With these corrections and the measured values of $\Delta_s H_T^o$ and of $\Delta_v H_T^o$ from Table 2, the standard molar enthalpies of vaporization $\Delta_v H^o$ or of sublimation $\Delta_s H^o$ at 298.15 K were calculated (Table 5). The enthalpies of fusion (Table 5) of compounds **B**, **D**, **F** and **G** were determined by DSC, their melting points are listed in Table 1.

The measurements of thermochemical properties of **B**–**D** were made for the first time. The investigation on the benzophenone has been a popular endeavor since 1931. For the value of enthalpy of formation $\Delta_f H_m^o$ (cr) of benzophenone the following results were measured by combustion calorimetry: -41.6 ± 6.3 kJ mol^{-1} [12], -32.3 ± 3.3 kJ mol^{-1} [13], and -34.5 ± 2.1 kJ mol^{-1} [14]. The measurement in this work value -42.21 ± 0.96 kJ mol^{-1} is in an acceptable agreement with earlier investigations. The derived value of the enthalpy of sublimation of **A** of 93.1 ± 2.2 kJ mol^{-1} is very close to the average of the earlier results surveyed by Chickos [15].

The only previous determination of the standard enthalpy of formation $\Delta_f H_m^o$(cr) of anthrone (**E**) has been made by El Watik and Sabbah [16] using combustion calorimetry. Their value $-79.9 \pm$ 2.1 kJ mol^{-1} was in the acceptable agreement with our value -85.0 ± 1.2 kJ mol^{-1}. The value of enthalpy of sublimation of **E** at 298.15 K $\Delta_s H^o = 103.32 \pm 0.63$ kJ mol^{-1} from the same work [16] is in agreement with our value 106.10 ± 0.81 kJ mol^{-1} too.

The enthalpies of combustion of compounds **F** and **G** have been measured earlier by Perisanu [17]. Derived there $\Delta_f H_m^o(\text{cr}) = -123.5 \pm 3.4$ kJ mol^{-1} of dibenzosuberone (**F**) was something embarrassing by its comparison with the value of $\Delta_f H_m^o(\text{cr}) = -37.2 \pm 14.0$ kJ mol^{-1} of substance (**G**) measured in the same work [17]. That was the reason to remeasure the enthalpy of combustion of compound (**F**) and additionally to measure the enthalpies of sublimation for both of compounds **F** and **G**. The measurement in this work value of $\Delta_f H_m^o(\text{cr}) = -48.8 \pm 1.1$ kJ mol^{-1} of dibenzosuberone was less anomalous than -123.5 kJ mol^{-1} [17] and lent itself to further interpretation.

The resulting interaction of structural elements in aromatic ketones could be assessed with the help of a group additivity procedure. We define the strain of a molecule H_s as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^o$(g) and the calculated sum of the strain-free increments of the Benson-type [3,4] for this molecule. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H_m^o$(g) of simple homologous ('strainless') molecules. The increments for alkanes [18], arenes [19], and ketones [2], necessary for this work, are already known (see Table 6). These increments were used to calculate the strain of the compounds investigated here. The estimated values of the strain enthalpies H_s for aromatic ketones are listed in Table 5. The result of the conjugation of the double

Table 6
Strain-free group increments [a] for calculation of the enthalpy of formation of aromatic ketones at 298.15 K (in kJ mol^{-1})

ΔH_{alkane} [18]		ΔH_{arene} [19]		ΔH_{ketone} [2]	
$CH_3[C]$	−42.05	$C_BH[2C_B]$	+13.7	$CH_3[CO]$	−42.05
$CH_2[2C]$	−21.46	$C_B[C, 2C_B]$	+23.5	$CH_2[CO, C]$	−21.76
CH[3C]	−9.04	$C_B[3C_B]$	+21.9 [4]	CH[CO, 2C]	−10.00
C[4C]	−1.26			C[CO, 3C]	+2.59

[a] C_B represents the C atom in a benzene ring. Group additivity value of CO[2C] = −130.54 kJ mol^{-1} [2]. Group additivity value of Ph[CO] = +86.61 kJ mol^{-1} [2].

bond of the carbonyl group with phenyl substituents in benzophenone leads to moderate destabilization of the molecule about 7.4 kJ mol^{-1}. In order to get a comparison with the cyclic aliphatic ketones, the strain enthalpies of cyclopentanone [1] ($\Delta_f H_m^o = -192.1 \pm 1.8$ and $H_s = 24.9$ kJ mol^{-1}), cyclohexanone [1] ($\Delta_f H_m^o = -226.1 \pm 2.1$ and $H_s = 12.3$ kJ mol^{-1}), and cycloheptanone [20] ($\Delta_f H_m^o = -231.3$ and $H_s = 28.6$ kJ mol^{-1}) were calculated from their standard enthalpies of formation in gaseous state at 298.15 K [1,20] and sum of the strain-free increments (Table 6). In the comparison with the strain of cyclopentanone, the conjugation of the phenyl substituent with the carbonyl group decreases the strain in 5-membered ring to 15.2 kJ mol^{-1} in 1-indanone. The introduction of the second phenyl ring on the 5-membered ring in 9-fluorenon return the strain of the ring on the level of 23.5 kJ mol^{-1}. A similar comparison for the 6-membered rings shows the absence of considerable interactions in α-tetralone ($H_s = 4.1$ kJ mol^{-1}), but the profound stabilization ($H_s = -19.7$ kJ mol^{-1}) was found for the anthrone. The interactions of the phenyl substituents and the carbonyl group on the 7-membered ring in dibenzosuberone (**F**) and 5,7-dihydro-6H-dibenzo[a,c]cyclohepten-6-one (**G**) in comparison with the strain (28.6 kJ mol^{-1}) of such a ring shows a slight increase of the strain, 40.7 and 32.1 kJ mol^{-1} respectively.

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