Research Article

Journal of Physical Organic Chemistry

Received: 22 October 2007, Revised: 4 December 2007, Accepted: 16 January 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1342

Standard molar enthalpies of formation of dimethylbenzophenones

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The standard ($p^0 = 0.1$ MPa) molar enthalpy of formation of 3,4-dimethylbenzophenone was derived from the standard molar energy of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry. The Calvet high temperature vacuum sublimation technique was used to measure the enthalpy of sublimation of the compound. From these experimental parameters, the standard molar enthalpy of formation of 3,4-dimethylbenzophenone, in the gaseous phase and at $T = 298.15$ K, was derived as $-(17.1 \pm 2.9)$ kJ mol^{-1}. Density functional theory was used to investigate the gas-phase molecular energetics of the 12 dimethylbenzophenones. Molecular geometries and vibrational frequencies were computed at the B3LYP/6-31G(d) level of theory. The larger 6-311+G(2d,2p) basis set was used to compute the energy of all dimethylbenzophenones and of the other compounds that were considered for the estimation of the standard molar enthalpies of formation at $T = 298.15$ K. The calculations show that the 2,2′- and 4,4′-dimethylbenzophenones are the least and most stable isomers, respectively. Finally, the calculated enthalpy of formation of the benzophenone that was also studied experimentally, 3,4-dimethylbenzophenone, is -16.7 kJ mol^{-1}, which is in excellent agreement with the experimental result. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: thermochemistry; enthalpy of formation; methylbenzophenone; density functional theory; combustion calorimetry; Calvet microcalorimetry

INTRODUCTION

The derivatives of benzophenone (diphenylketone) are important intermediates for manufacturing high-value products that can be drugs, dyes, inks or pesticides and are also used for the absorption of UV radiation in skin protectors.[1–7] Furthermore, they are also used in the protection of other materials, such as plastics, perfumes or cosmetics, by acting as UV light stabilizers and by preventing the formation of free radicals.

Despite their wide range of applications and importance, only a few studies may be found in the literature concerning the thermochemistry of benzophenone derivatives: Inagaki *et al.* [8] used a static bomb calorimeter to determine the enthalpy of combustion of the solid 2,4,6-triisopropyl benzophenone and measured its vapour pressures with the aim of determining its enthalpy of sublimation; Colamina *et al.*[9] also used static bomb calorimetry to determine the standard molar enthalpy of formation of crystalline 4-methylbenzophenone; Ribeiro da Silva *et al.*[10,11] used a combination of experimental and computational approaches for the study of the molecular energetics of the three monomethylbenzophenones and of all possible monochloro and dichlorobenzophenones. No other thermochemical data were found for other benzophenone derivatives.

This work reports the standard ($p^0 = 0.1$ MPa) molar enthalpy of formation in the condensed state, at $T = 298.15$ K, for 3,4-dimethylbenzophenone. The value was derived from the experimental determination, by static bomb calorimetry, of its energy of combustion and the standard molar enthalpy of sublimation, which was measured by high temperature Calvet calorimetry. Also presented is a computational study of the molecular energetics of all dimethylbenzophenones either with two methyl groups attached to the same ring or with a methyl group attached to each aromatic ring. There are six possible isomers for each case with the following names: 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethylbenzophenone when the two methyl groups share a single ring of the parent benzophenone compound, and 2,2′-, 2,3′-, 2,4′-, 3,3′-, 3,4′- and 4,4′- dimethylbenzophenone in the cases where there is a single methyl group per ring.

EXPERIMENTAL DETAILS

Materials

3,4-Dimethylbenzophenone [CAS 2571-39-3], studied in this work, was obtained commercially from Aldrich Chemical Co. with

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a nominal mass fraction purity of 0.99. The compound was purified by repeated sublimation under reduced pressure until the combustion results were consistent and the carbon dioxide recovery ratios in the combustion experiments were satisfactory. The average ratio of the mass of carbon dioxide recovered to that calculated from the mass of sample, together with the standard deviation of the mean was (1.0003 ± 0.020). The specific density of the sample was estimated as the average of the two literature values for 4-methylbenzophenone,[12,13] as $\rho = 1.176\ \mathrm{g\ cm^{-3}}$.

Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system. The bomb calorimeter, subsidiary apparatus and technique have been described previously in the literature.[14,15]

Combustion of certificated benzoic acid NBS standard reference material, sample 39j, was used for the calibration of the bomb. Its massic energy of combustion is $-(26\,434 \pm 3)\ \mathrm{J\ g^{-1}}$, under certificate conditions.[16] The calibration results were corrected to give the energy equivalent ε (calor) corresponding to the average mass of water added to the calorimeter: 3119.6 g. From six calibration experiments, ε (calor) = (15 905.7 ± 0.96) $\mathrm{J\ K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean.

In all combustion experiments, 1.00 $\mathrm{cm^3}$ of water was introduced into the bomb, a twin-valve static combustion bomb, type 1105 from Parr Instrument Company, made of stainless steel, with an internal volume of 0.340 $\mathrm{cm^3}$. The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

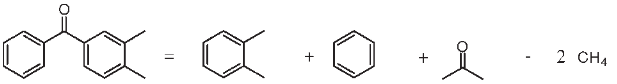
For all experiments, the calorimeter temperatures were measured to $\pm(1 \times 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. After the start of the experiment at least 100 readings, at time intervals of 10 s, were taken, followed by the ignition of the crystalline sample in the pellet form which was made at $T = (298.150 \pm 0.001)$ K, by the discharge of a 1400 μF capacitor through the platinum ignition wire; after the ignition, 100 readings were taken for both the main and after periods.

For the cotton thread fuse of empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, the massic energy of combustion was assigned to $-\Delta_c u^0 = 16\,240\ \mathrm{J\ g^{-1}}$,[17] a value that has been confirmed in our laboratory. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. The corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ\ mol^{-1}}$,[18] for the molar energy of formation of 0.1 mol $\mathrm{dm^{-3}}$ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2}$, $\mathrm{O_2}$ and $\mathrm{H_2O(l)}$. All the necessary weighings were made in a Mettler AE 240 microbalance, sensitivity $\pm(1 \times 10^{-6})$ g; corrections from apparent mass to true mass were made. An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2\ \mathrm{J\ g^{-1}\ MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds,[19] was assumed. The massic energy of combustion, $\Delta_c u^0$, was calculated by the procedure given by Hubbard *et al.*[20] The amount of 3,4-dimethylbenzophenone used in each experiment was determined from the total mass of carbon dioxide produced during the experiments (Mettler Toledo AT 201 balance, sensitivity $\pm(1 \times 10^{-5})$ g) taking into account that formed from the combustion of the cotton thread fuse.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005.[21]

Microcalorimetry Calvet

The standard molar enthalpy of sublimation of 3,4-dimethylbenzophenone was measured using the vacuum sublimation drop-microcalorimetric technique.[22,23] The apparatus and technique were recently described.[23] Samples of about 3–6 mg of the crystalline compound, contained in a small thin glass capillary tube sealed at one end, and a blank capillary with similar mass, were simultaneously dropped at room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter (Setaram HT 1000), held at $T = 401$ K, and then removed from the hot zone by vacuum sublimation. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ±10 μg, into each of the twin calorimeter cells. The observed enthalpy of sublimation $\Delta_{\mathrm{cr},298.15\,\mathrm{K}}^{\mathrm{g},401\,\mathrm{K}}H_{\mathrm{m}}$ was corrected to $T = 298.15$ K using values of $\Delta_{298.15\,\mathrm{K}}^{401\,\mathrm{K}}H_{\mathrm{m}}^0(\mathrm{g})$ estimated by a group method including *o*-xylene, benzene, acetone and methane species, Eqn 1, based on data of Stull *et al.*[24] For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpies of sublimation of naphthalene (72.6 ± 0.6) $\mathrm{kJ\ mol^{-1}}$,[25] at $T = 298.15$ K.



(1)

COMPUTATIONAL DETAILS

In the present work, the same computational density functional theory approach used in previous studies dealing with substituted benzophenones was used.[10,11] In those works, the B3LYP method – Becke's three-parameter hybrid functional using the non-local correlation due to Lee *et al.*[26,27] – was combined with two different basis sets. The 6-31G(d) basis set was used for the optimization of the geometry of all compounds and also for the calculation of vibrational frequencies. The calculation of the frequencies permitted the confirmation that all optimized geometries were true minima on the potential energy surface, and the correction of the energies calculated with the larger 6-311+G(2d,2p) basis set for $T = 298.15$ K. All these calculations have been performed by means of the Gaussian 98 computer code.[28]

RESULTS AND DISCUSSION

Results for the combustion experiments of the compound are given in Table 1, where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned to ε (calor), and ΔU_Σ is the energy correction to the standard state. The remaining quantities are as previously defined.[20] For the static bomb measurements, as samples were ignited at $T = (298.150 \pm 0.001)$ K

$$\Delta U(\mathrm{IPB}) = -\{\varepsilon_{\mathrm{calor}} + \Delta m(\mathrm{H_2O})c_{\mathrm{p}}(\mathrm{H_2O,l}) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign}) \tag{2}$$

where $\Delta U(\mathrm{IBP})$ is the energy associated to the isothermal bomb process, ε_{f} the energy of the bomb contents after ignition,

Table 1. Results of combustion experiments at $T = 298.15$ K

	1	2	3	4	5	6	7
m(cpd) (g)	0.66648	0.59665	0.60988	0.59728	0.59980	0.60415	0.58587
m'(fuse) (g)	0.00240	0.00255	0.00231	0.00241	0.00243	0.00260	0.00281
ΔT_{ad} (K)	1.55118	1.38854	1.41831	1.38997	1.39554	1.40571	1.36408
ε_f (J K^{-1})	16.30	16.06	16.22	16.19	16.19	16.21	15.87
$\Delta m(H_2O)$ (g)	0.0	0.1	0.0	0.0	0.0	0.0	0.0
$-\Delta U$(IBP) (J)^a	24 696.70	22 107.40	22 581.05	22 129.79	22 218.46	22 380.45	21 717.18
ΔU(fuse) (J)	38.98	41.41	37.51	39.14	39.46	42.22	45.63
$\Delta U(HNO_3)$ (J)	9.19	8.06	0.32	0.28	0.31	0.33	0.34
ΔU(ign) (J)	1.19	1.18	1.17	1.16	1.17	1.14	1.12
ΔU_Σ (J)	13.89	12.26	12.53	12.25	12.31	12.39	12.00
$-\Delta_c u^0$ (J g^{-1})	36 962.31	36 949.08	36 942.82	36 964.44	36 956.29	36 953.59	36 969.31

m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion.

[a] ΔU(IBP) already includes the ΔU(ign).

Table 2. Derived standard molar energy $\Delta_c U_m^0$, standard molar enthalpy of combustion $\Delta_c H_m^0$ and standard molar enthalpy of formation $\Delta_f H_m^0$ for 3,4-dimethylbenzophenone, 3,4-DMBZPH, at $T = 298.15$ K with $p^0 = 0.1$ MPa

	$\Delta_c U_m^0\ (cr)$ (kJ mol^{-1})	$\Delta_c H_m^0\ (cr)$ (kJ mol^{-1})	$\Delta_f H_m^0\ (cr)$ (kJ mol^{-1})
3,4-DMBZPH	-7771.1 ± 2.0	-7778.5 ± 2.0	-125.0 ± 2.8

ΔU(ign) the ignition energy and ΔT_{ad} is the adiabatic temperature rise.

The individual values of the massic energies of combustion, $-\Delta_c u^0$, yield the mean value, $\langle \Delta_c u^0 \rangle = -(36\,956.8 \pm 3.5)$ J g^{-1}, where the uncertainty is the standard deviation. Here, $\Delta_c u^0$ refers to the idealized combustion reaction yielding $CO_2(g)$ and $H_2O(l)$ according to

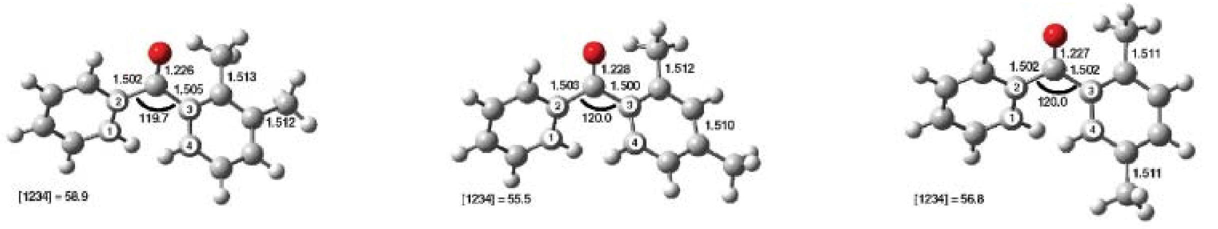
$$C_{15}H_{14}O(cr) + 18\,O_2(g) \rightarrow 15\,CO_2(g) + 7\,H_2O(l) \qquad (3)$$

Table 2 lists the derived standard molar energy and enthalpy of combustion and standard molar enthalpy of formation for the 3,4-dimethylbenzophenone in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical practice,[29,30] the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used. To derive $\Delta_f H_m^0(cr)$ from $\Delta_c H_m^0(cr)$, the standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$, at $T = 298.15$ K, $-(393.51 \pm 0.13)$ kJ mol^{-1},[31] and $-(285.830 \pm 0.042)$ kJ mol^{-1},[31] respectively, were used.

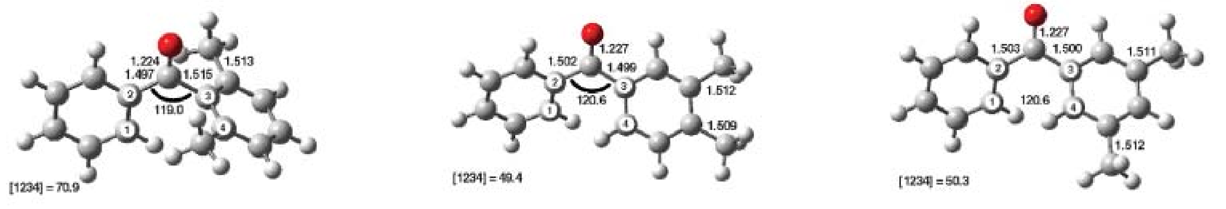
Measurements of the standard molar enthalpy of sublimation of 3,4-dimethylbenzophenone, by microcalorimetry, as well the respective uncertainty, taken as twice the standard deviations of the mean, are given in Table 3. The combination of the derived standard molar enthalpy of formation in the condensed phase with the standard molar enthalpy of sublimation yields the

Table 3. Microcalorimetric standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation, at $T = 298.15$ K, for 3,4-dimethylbenzophenone

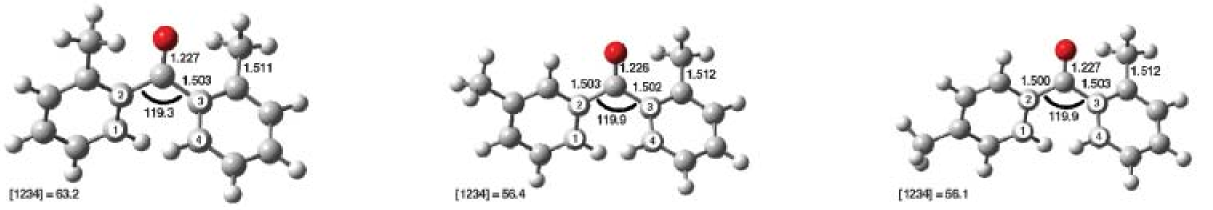
	Number of experiments	T (K)	$\Delta_{cr}^{g,T} H_m^0\ (T)$ (kJ mol^{-1})	$\Delta_{298.15K}^{T} H_m^0\ (g)$ (kJ mol^{-1})	$\Delta_{cr}^{g} H_m^0$ (298.15 K) (kJ mol^{-1})
3,4-DMBZPH	6	401	134.5 ± 0.8	26.6	107.9 ± 0.8



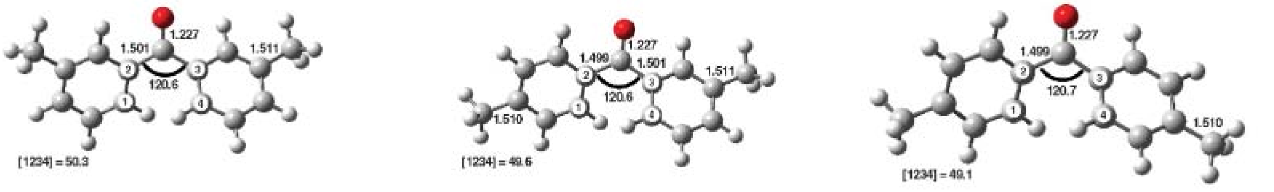
2,3-dimethylbenzophenone 2,4-dimethylbenzophenone 2,5-dimethylbenzophenone



2,6-dimethylbenzophenone 3,4-dimethylbenzophenone 3,5-dimethylbenzophenone



2,2'-dimethylbenzophenone 2,3'-dimethylbenzophenone 2,4'-dimethylbenzophenone



3,3'-dimethylbenzophenone 3,4'-dimethylbenzophenone 4,4'-dimethylbenzophenone

Figure 1. Optimized most stable configurations for the dimethylbenzophenones. Selected distances are in Å and angles in degrees.

standard molar enthalpy of formation, at $T = 298.15$ K, in the gaseous phase for 3,4-dimethylbenzophenone as $\Delta_f H_m^0(g) = -(17.1 \pm 2.9)\ \text{kJ mol}^{-1}$.

The B3LYP/6-31G(d) approach was used for the full optimization of the structures of all possible dimethylbenzophenones. The most stable final states are depicted in Fig. 1 together with some selected geometrical parameters. The most striking difference found between the calculated distances and angles for the different isomers is related to the torsion of the phenyl rings with respect to each other and also to the C=O bond; the torsion is measured in Fig. 1 by the CCCC dihedral angle involving atoms 1–4. As expected, due to the interaction between the methyl substituents and the carbonyl bond, the torsion is greater in the cases where the CH_3 groups are attached in the *ortho* position with the C=O bond, reaching a maximum value in the case of 2,6-dimethylbenzophenone. In the latter situation, the plane of the double substituted ring is normal to the plane passing through C_3—C=O. If the methyl groups are also attached in *ortho* positions but in different rings, that is in the case of 2,2′-dimethylbenzophenone, the calculated CCCC angle lies between the values found for 2,6-dimethylbenzophenone and for the different 2,*N*-dimethylbenzophenones (*N* = 3, 4, 3′ and 4′).

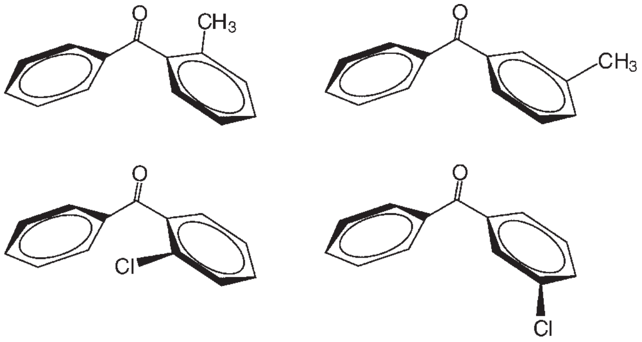


Figure 2. Most stable geometries for the introduction of chlorine and methyl groups entering positions 2 and 3 in benzophenone.

In the other cases, where the methyl groups enter at *meta* or *para* positions in the aromatic ring(s), the CCCC dihedral angles are ~50°; notice that the CCCC angle calculated for benzophenone is 50.0°.[10,11]

When compared with the structures previously optimized for the dichlorobenzophenones,[11] the most stable conformations found for the dimethylbenzophenones present the methyl groups syn to the C=O bond, while that is not the case with the chlorinated compounds where the chlorine atoms prefer to be anti to the carbonyl group as shown in Fig. 2. This suggests that the steric interaction between the chlorine and the carbonyl group is much more destabilizing than that found between chlorine and the opposite ring; a reverse order is found for the methyl derivatives of benzophenone.

The consideration of the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) enthalpies for all dimethylbenzophenones (given as Supplementary Material) shows that the least stable dimethylbenzophenone is the 2,2′-isomer while the 4,4′ doubly methylated benzophenone is the most stable of the compounds studied.

The enthalpies of formation of all the dimethylbenzophenones were estimated by using the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) approach to compute the enthalpies of the following reactions:

$$\text{dimethylbenzophenone} + 2\,\text{benzene} \rightarrow \text{benzophenone} + 2\,\text{toluene} \tag{4}$$

$$\text{dimethylbenzophenone} + \text{benzene} \rightarrow \text{benzophenone} + \textit{ortho}-\text{xylene} \tag{5}$$

$$\text{dimethylbenzophenone} + \text{benzene} \rightarrow \text{benzophenone} + \textit{meta}-\text{xylene} \tag{6}$$

$$\text{dimethylbenzophenone} + \text{benzene} \rightarrow \text{benzophenone} + \textit{para}-\text{xylene} \tag{7}$$

and by considering the experimental standard molar enthalpies of formation in the gas-phase, $T = 298.15$ K, of benzene, $\Delta_f H^0_m = (82.6 \pm 0.7)$ kJ mol^{-1} (g),[32] of benzophenone, $\Delta_f H^0_m(g) = (49.9 \pm 3.0)$ kJ mol^{-1},[33] of toluene (methylbenzene), $\Delta_f H^0_m(g) = (50.5 \pm 0.5)$ kJ mol^{-1},[32] of *ortho*-xylene (1,2-dimethylbenzene), $\Delta_f H^0_m(g) = (19.0 \pm 1.1)$ kJ mol^{-1},[33,34] of meta-xylene (1,3-dimethylbenzene), $\Delta_f H^0_m(g) = (17.2 \pm 0.8)$ kJ mol^{-1},[33,34] and of para-xylene (1,4-dimethylbenzene), $\Delta_f H^0_m(g) = (17.9 \pm 1.0)$ kJ mol^{-1}.[33,34] Reaction (4) was used to estimate the enthalpies of formation of the compounds with a methyl group in each ring while Reactions (5)–(7) were used to estimate the enthalpies of formation of the compounds with two methyl groups inserted in the same ring. More precisely, Reaction (5) was used to estimate the enthalpies of formation of 2,3- and 3,4-dimethylbenzophenones, Reaction (6) was used for the 2,4-, 2,6- and 3,5-dimethylbenzophenones compounds and, finally, Reaction (7) was used for the 2,5-dimethylbenzophenone isomer. The enthalpies of reaction calculated for each of the dimethylbenzophenones are reported in Table 4 together with the estimated enthalpies of formation.

Most importantly, the calculated result for the 3,4-dimethylbenzophenone is in excellent agreement with the experimental value, the difference between these two quantities being only 0.4 kJ mol^{-1}. In fact, the calculated result is within the uncertainty interval associated with the experimental one.

Table 4. Computed enthalpies of the working reactions (ΔH_R) used to calculate the enthalpies of formation (ΔH_f) of the 12 dimethylbenzophenones

Compound	Reaction	ΔH_R	ΔH_f
2,3-Dimethylbenzophenone	5	−11.0	−2.7
2,4-Dimethylbenzophenone	6	−5.1	−10.4
2,5-Dimethylbenzophenone	7	−6.5	−8.3
2,6-Dimethylbenzophenone	6	−14.4	−1.1
3,4-Dimethylbenzophenone	5	3.0	−16.7
3,5-Dimethylbenzophenone	6	1.0	−16.5
2,2′-Dimethylbenzophenone	4	−19.6	4.3
2,3′-Dimethylbenzophenone	4	−10.9	−4.4
2,4′-Dimethylbenzophenone	4	−9.3	−6.0
3,3′-Dimethylbenzophenone	4	−2.9	−12.4
3,4′-Dimethylbenzophenone	4	−1.6	−13.7
4,4′-Dimethylbenzophenone	4	−0.6	−14.7

Values are in kJ mol^{-1}.

Table 5. Enthalpic increments for the double methylation of benzophenone and benzoic acid

	X = Benzophenone		X = Benzoic acid		
Compound	$\Delta_f H_m^0$ (g)	Δ(methylation)	$\Delta_f H_m^0$ (g)	Δ(methylation)	Δ Δ[b]
X	49.9 ± 3.0[33]		−294.4 ± 0.7[33,36,37]		
2,3-$(CH_3)_2$X	−2.7[a]	52.6	−345.8 ± 1.7[33]	51.4 ± 1.8	−1.2
2,4-$(CH_3)_2$X	−10.4[a]	60.3	−355.0 ± 1.7[33]	60.6 ± 1.8	0.3
2,5-$(CH_3)_2$X	−8.3[a]	58.2	−351.1 ± 1.7[33]	56.7 ± 1.8	−1.5
2,6-$(CH_3)_2$X	−1.1[a]	51.0	−341.6 ± 1.7[33]	47.2 ± 1.8	−3.8
3,4-$(CH_3)_2$X	−16.7[a]	66.6	−362.4 ± 1.7[33]	68.0 ± 1.8	1.4
3,5-$(CH_3)_2$X	−16.5[a]	66.4	−364.5 ± 1.7[33]	70.1 ± 1.8	3.7

Values are in kJ mol^{-1}.

[a] Estimated values from this work.

[b] Difference between the enthalpies of methylation of the different dimethylbenzoic acids and similarly substituted dimethylbenzophenones.

Therefore, this close agreement suggests that the computational approach used is reliable for the purposes of the present study and the estimates for the other dimethylbenzophenones may be considered as good estimates for the enthalpies of formation of these compounds. As it can be seen from the results reported in Table 4, there are several compounds for which similar enthalpies of formation were estimated; further, the difference between the most stable and the least stable isomer is 21 kJ mol^{-1}. As a result of the similar torsion of the rings with respect to the carbonyl group for 3,4-, 3,5-, 3,3′-, 3,4′- and 3,5′-dimethylbenzophenones when compared with unsubstituted benzophenone, these dimethyl isomers are those for which a more negative enthalpy of formation is estimated. However, the torsion of the rings is not the only cause for the destabilization of the compounds since 2,6-dimethylbenzophenone is not the least stable species, probably suggesting that there is a better electron delocalization in one of the unsubstituted rings in the case of the 2,6-dimethyl compound, when compared with the 2,2′-dimethyl isomer where there is a methyl group per aromatic ring. Despite the different positioning of the chlorine substituents in 2,2′-dichlorobenzophenone, as shown in Fig. 2, the latter species was also the least stable of the dichlorobenzophenones. However, in that work, the 4,4′-dichlorobenzophenone was the most stable isomer while in the case of the dimethylbenzophenones, double substitutions at positions 3 and 4 or 3 and 5 are slightly preferred. Nevertheless, this analysis is difficult since the differences between the enthalpies calculated for the compounds listed above are smaller than the uncertainty that may affect thermodynamic values computed with the B3LYP approach,[10,11] despite the fact that in the present work the same computational methodology yielded an excellent estimate of the standard molar enthalpy of formation in the gas-phase for the 3,4-dimethylbenzophenone compound.

The enthalpic variations for the insertion of two methyl groups in the same ring of benzophenone are compared with the enthalpic increments for methyl insertion at similar positions in the ring of benzoic acid. These increments are compiled in Table 5. The smallest Δ value when X is benzophenone is found for 2,6-dimethylbenzophenone while the higher one is found for the 3,4-isomer. The analysis of the results reported in Table 5 shows similar Δ values when X is benzophenone or benzoic acid, which is much more evident if one considers the ΔΔ values given in the last column of Table 5. These findings suggest that the carbonyl group has a similar role both in the ketone and in the acid, that is the carbonyl group has the ability to accommodate incoming charge from the contiguous methyl groups. Recently, it was observed in 2-*R*-3-methylquinoxaline-1,4-dioxides that the presence of electron donors (X is benzyl) or electron acceptors (X is *p*-nitrobenzyl) in *R* = —C(=O)X substituents has similar effects on the electronic density of the quinoxaline ring. In fact, identical N—O bond dissociation enthalpies were calculated for 2-benzoyl-3-methylquinoxaline-1,4-dioxide and 2-*p*-nitrobenzoyl-3-methylquinoxaline-1,4-dioxide.[35] Furthermore, the computed N—O bond dissociation enthalpies in 2-*tert*-butoxycarbonyl-3-methylquinoxaline-1,4-dioxide are also close to the values calculated for 2-benzoyl-3-methylquinoxaline-1,4-dioxide suggesting that the different kinds of effects (mesomeric or inductive) associated with the substituents introduced at the position 2 of the quinoxaline ring affect neither the electronic nor the structure of the heteroatomic ring.

From the experimental standard gas-phase enthalpies of formation of toluene, benzene and benzophenone given above, the standard molar enthalpy of formation of 3,4-dimethylbenzophenone can be also estimated from the standard molar enthalpy of gaseous benzophenone, (49.9 ± 3.0) kJ mol^{-1}, by adding twice the value for the increment in enthalpy for methyl substitution into benzene, that is −(32.1 ± 0.9) kJ mol^{-1}. The estimated value is $\Delta_f H_m^0(g) = -(14.3 \pm 3.1)$ kJ mol^{-1}, which is in good agreement with the experimental result.

SUPPLEMENTARY MATERIAL

Table SM1 with the absolute enthalpies calculated for all compounds considered in the present work. This material is available free of charge in Wiley Interscience.

Acknowledgements

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for financial support to Centro de Investigação em Química, University of Porto. L.M.P.F.A and

J.R.B.G. thank FCT and the European Social Fund (ESF), under the Community Support Framework (CSF), for the award of post-doctoral fellowships, respectively (SFRH/BPD/25490/2005) and (SFRH/BPD/24676/2005).

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