# Experimental and Computational Studies on the Molecular Energetics of Chlorobenzophenones

**Manuel A. V. Ribeiro da Silva,\* Luísa M. P. F. Amaral, and José R. B. Gomes**

*Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal*

The standard ($p° = 0.1$ MPa) molar enthalpies of formation, $\Delta_f H_m°$, of crystalline 2-, 3- and 4-chlorobenzophenone and 4,4′-dichlorobenzophenone were derived from the standard molar energies of combustion, $\Delta_c U_m°$, in oxygen, to yield $CO_2(g)$, $N_2(g)$, and $HCl \cdot 600H_2O(l)$, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The Calvet high-temperature vacuum sublimation technique was used to measure the enthalpy of sublimation, $\Delta_{cr}^g H_m°$, of the compound 2-chlorobenzophenone. For the other three compounds, the standard molar enthalpies of sublimation, at $T = 298.15$ K were derived by the Clausius–Clapeyron equation, from the temperature dependence of the vapor pressures of these compounds, measured by the Knudsen-effusion technique. From the values of $\Delta_f H_m°$ and $\Delta_{cr}^g H_m°$, the standard molar enthalpies of formation of all the compounds, in the gaseous phase, $\Delta_f H_m°(g)$, at $T = 298.15$ K, were derived. These values were also calculated by using the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) computational approach.

## 1. Introduction

The compounds studied in the present work are important intermediates in the manufacturing of important drugs. In fact, the benzodiazepines, which are psychoactive drugs are used as tranquilizers with several different specific properties, are derived from chlorinated benzophenones.[1,2] Significant examples are Diazepam (a 2-substituted amino derivative of 5-chlorobenzophenone), Clonazepam (a 2-substituted amino and 5-nitro derivative of 2-chlorobenzophenone), and Alprazolam (a 2-substituted 1,3,4-triazole derivative of 5-chlorobenzophenone) among others. As happens with other ketones, the hydrogenation of chlorobenzophenones is also used as a means to obtain the corresponding alcohols which are commonly used in industry. For example, several reaction procedures are employed to reduce 4-chlorobenzophenone to 4-chlorobenzhydrol,[3,4] which suffers some more synthetic modifications for the production of the antitussive Clophedianol compound.

In this work, the molecular energetics of three monochlorinated benzophenones and a dichlorobenzophenone were studied by means of rotating bomb combustion calorimetry, Calvet microcalorimetry, and experiments based on the Knudsen effusion method. The gas-phase standard molar enthalpies of formation of the remaining mono and dichlorobenzophenones were determined by means of density functional theory based calculations. The choice of these molecules is due to the fact that the effects of the introduction of chlorine atoms in benzene rings[5–11] as well as the effect of the same substituents into heterocycles[12–17] has been, for some years, one of our research objectives on thermochemical properties.

As written above, rotating bomb combustion calorimetry was one of the techniques used in this work aiming at the measurement of the standard ($p° = 0.1$ MPa) molar energies of combustion, in oxygen, at $T = 298.15$ K, for 2-, 3-, and 4-chlorobenzophenones and also of 4,4′-dichlorobenzophenone.

Their standard molar enthalpies of sublimation, at the same temperature, were obtained by using Calvet microcalorimetry for 2-chlorobenzophenone while the Knudsen effusion method was used to study the 3- and 4-chlorobenzophenones and 4,4′-dichlorobenzophenone. The derived standard molar enthalpies of formation, in the gaseous state, at $T = 298.15$ K, were compared with values calculated by using the density functional theory.

## 2. Experimental Details

The compounds 2-chlorobenzophenone (2-Clbzph, [CAS 5162–03-8]), 3-chlorobenzophenone (3-Clbzph, [CAS 1016–78-0]), 4-chlorobenzophenone (4-Clbzph, [CAS 134–85-0]), and 4,4′-dichlorobenzophenone (4,4′-Cl₂bzph, [CAS 90–98-2]) were obtained commercially from Aldrich Chemical Co. and were purified by repeated sublimation under reduced pressure. The specific densities, used to calculate the true mass from apparent mass in air were, $\rho = 1.00$ g·cm⁻³ for 2-Clbzph, $\rho = 0.966$ g·cm⁻³ for 3-Clbzph, $\rho = 1.09$ g·cm⁻³ for 4-Clbzph, and $\rho = 1.19$ g·cm⁻³ for 4,4′-Cl₂bzph, determined from the ratio mass/volume of pellets of the compounds.

The combustion experiments were performed with an iso-peribol rotating-bomb calorimeter, developed by Sunner[18] at the University of Lund, Sweden. The apparatus and the technique have been described in the literature.[19,20] The bomb, whose internal volume is 0.258 dm³, is of stainless steel lined with platinum, with the internal fittings machined from platinum. In each experiment, the bomb is suspended from the lid of the calorimeter can, to which 5222.5 g of water, previously weighed in a perspex vessel, is added. For each experiment, a correction to the energy equivalent was made for the deviation of the mass of water used to the reference mass of 5222.5 g.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K at time intervals of 10 s, using a Hewlett–Packard (HP-2804A) quartz thermometer interfaced to a PC programmed to compute the corrected temperature change. For each experiment, the ignition

* Corresponding author. Phone: +351 2 20402 521. Fax: +351 22 0402 522. E-mail: risilva@fc.up.pt.

temperature was chosen so that the final temperature would be close to 298.15 K. Fore-period and after-period readings were taken for about 20 min, and the main-period was about 25 min. Data acquisition and control of the calorimeter were performed through the use of the LABTERMO program.[21]

The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature rise in the main-period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, as described by Good et al.,[22] the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket.

The isothermal jacket consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature close to 303.5 K, controlled with a precision of $10^{-3}$ K using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant-temperature enclose.

Benzoic acid, NBS Standard Reference Material, Sample 39i, was used for the calibration of the bomb. Its massic energy of combustion is $-26434 \pm 3$ J·g$^{-1}$, under certificate conditions. Calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa, with 1.00 cm$^3$ of water added to the bomb. From six calibrations experiments, the value of the energy equivalent of the calorimeter was found to be $\epsilon$ (calor) = 25165.8 ± 1.7 J·K$^{-1}$. This value was used for the experiments carried out for the 4-Clbzph compound. Then, since the equipment was stopped for maintenance works, a new calibration constant of $\epsilon$ (calor) = 25165.6 ± 1.5 J·K$^{-1}$ was used for the other compounds. The uncertainty quoted for the calibration constants is the standard deviation of the mean.

The crystalline compounds were burnt in pellet form. The combustion experiments were carried out in oxygen at a pressure of 3.04 MPa in the presence of an aqueous solution of As$_2$O$_3$, in order to reduce to hydrochloric acid all of the free chlorine produced by the combustion. For the singly chlorinated compounds, 15.00 cm$^3$ of aqueous As$_2$O$_3$ ≈ 0.09 mol·dm$^{-3}$ was used, whereas for the dichlorobenzophenone studied experimentally, 25.00 cm$^3$ of aqueous As$_2$O$_3$ ≈ 0.09 mol·dm$^{-3}$ was used. The extent of oxidation of As$_2$O$_3$(aq) was determined by titration with standardized iodine solution. For the calculation of the energetic term $\Delta U$(As$_2$O$_3$), corresponding to the energy of oxidation of As$_2$O$_3$ to As$_2$O$_5$ in aqueous solution, the procedure described by Hu et al.,[23] as well as the enthalpies of oxidation of As$_2$O$_3$(aq) by Cl$_2$,[24] and the thermal effects of mixing As$_2$O$_5$ (aq) with strong acids were used.[25] Within the precision of the analytical method, no evidence was found for the oxidation of the aqueous solution of As$_2$O$_3$ after the bomb had been charged with oxygen at $p$ = 3.04 MPa and left up to 5 h at room temperature.[5,19]

The electrical energy for ignition was determined from the change in potential difference across a 1400 $\mu$F condenser discharge through a platinum wire of diameter 0.05 mm.

The amount of H$_2$PtCl$_6$(aq) was determined from the loss of mass from the platinum crucible and its supporting parts. The energy correction was based on $\Delta_f H_m^\circ$ (H$_2$PtCl$_6$, aq) = $-676.1$ ± 0.1 kJ·mol$^{-1}$.[26] For the cotton thread fuse, whose empirical formula is CH$_{1.686}$O$_{0.843}$, $\Delta_c u^\circ = -16240$ J·g$^{-1}$ was used,[27] a value previously confirmed in our laboratory.

The nitric acid formed was determined using the Devarda's alloy method[28] and corrections were based on $-59.7$ kJ·mol$^{-1}$ for the molar energy of formation in which 0.1 mol·dm$^{-3}$ HNO$_3$(aq) is formed from O$_2$(g), N$_2$(g), and H$_2$O(l).[26] An estimated value of the pressure coefficient of massic energy: $(\partial u/\partial p)_T = -0.2$ J·g$^{-1}$·MPa$^{-1}$ at $T$ = 298.15 K, a typical value for most organic compounds,[29] was assumed for all chlorobenzophenones. For each compound, the standard state corrections, $\Delta U_\Sigma$, and the heat capacities of the bomb contents, $\epsilon_i$ and $\epsilon_f$, were calculated by the procedure given by Hubbard et al.[30] using the solubility constants and energies of solution of CO$_2$ and O$_2$, as given by Hu et al.[23]

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005.[31]

The standard molar enthalpy of sublimation of 2-chlorobenzophene was measured using the "vacuum sublimation" drop microcalorimetric method.[32,33] Samples of about 3−5 mg of crystalline compound, contained in a small thin glass capillary tube sealed at one end, and a blank capillary with nearly the same mass were simultaneously dropped at room temperature into the hot reaction vessels in the Calvet high-temperature microcalorimeter (Setaram HT 1000) set at 401.2 K. An endothermic peak due to the heating of the sample from room temperature to the temperature of the calorimeter was first observed. After the signal returned to the baseline, the sample was removed from the hot zone by vacuum. 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 $\mu$g, into each of the twin calorimeter cells.

The observed enthalpies of sublimation $\Delta_{cr, 298.15K}^{g,T} H_m^\circ$, were corrected to $T$ = 298.15 K using values of $\Delta_{298.15K}^{T} H_m^\circ$(g) estimated by a group-additivity method based on data of Stull et al.,[34] where $T$ is the temperature of the hot reaction vessel. The microcalorimeter was calibrated in situ for these measurements using the reported standard molar enthalpy of sublimation of naphthalene 72.6 ± 0.6 kJ·mol$^{-1}$.[35]

The mass-loss Knudsen effusion method was used to measure the vapor pressures, as a function of temperature of the 3-Clbzph and 4-Clbzph, and 4,4′-Cl$_2$bzph. The Knudsen effusion apparatus enables the simultaneous operation of nine aluminum effusion cells.[36] This apparatus has been tested by measuring vapor pressures between 0.1 and 1 Pa, over temperature ranges of ca. 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene.[36] The nine effusion cells are contained in cylindrical holes inside three aluminum blocks, three cells per block. Each block is kept at a constant temperature, different from the other two blocks. The effusion cells are weighed before and after each effusion time period, $t$, to determine the mass loss, $\Delta m$, of the samples. At the temperature $T$ of the experiment, the vapor pressure $p$ is calculated by the equation

$$p = (\Delta m/A_0 w_0 t) \cdot (2\pi RT/M)^{1/2} \qquad (1)$$

where $M$ is the molar mass of the effusing vapor, $R$ is the gas constant, $A_0$ is the area of the effusion hole, and $w_0$ is the respective Clausing factor calculated by the equation

$$w_0 = \{1 + (3l/8r)\}^{-1} \qquad (2)$$

where $l$ is the thickness of the effusion hole and $r$ its radius. The thickness of the effusion holes were 0.0125 mm; the areas and Clausing factors are given as Supporting Information. The

Molecular Energetics of Chlorobenzophenones

*J. Phys. Chem. B, Vol. 111, No. 45, 2007* **13035**

**TABLE 1: Results of Typical Combustion Experiments at $T = 298.15$ K**

|  | 2-Clbzph | 3-Clbzph | 4-Clbzph | 4,4′-Cl₂bzph |
|---|---|---|---|---|
| $m$(cpd)/g | 0.72246 | 0.72510 | 0.73993 | 0.75818 |
| $m'$(fuse)/g | 0.00273 | 0.00280 | 0.00279 | 0.00301 |
| $\Delta T_{ad}$/K | 0.84615 | 0.84653 | 0.86392 | 0.74853 |
| $\epsilon_i$/(J·K$^{-1}$) | 72.68 | 72.78 | 72.69 | 93.73 |
| $\epsilon_f$/(J·K$^{-1}$) | 71.86 | 71.79 | 71.81 | 91.62 |
| $\Delta m$(H₂O)/g | 0.4 | 0.8 | −0.8 | 0.6 |
| $-\Delta U$(IBP)/J$^a$ | 21355.51 | 21366.70 | 21799.89 | 18908.00 |
| $\Delta U$(fuse)/J | 44.34 | 45.47 | 45.31 | 48.88 |
| $\Delta U$(HNO₃)/J | 12.06 | 6.21 | 8.36 | 6.93 |
| $\Delta U$(As₂O₃)/J | 60.62 | 68.17 | 73.25 | 138.99 |
| $\Delta U$(ign)/J | 1.29 | 1.19 | 1.27 | 1.28 |
| $\Delta U$((H₂PtCl₆)/J | 0.73 | 0.55 | 0.82 | 1.54 |
| $\Delta U_\Sigma$/J | 35.60 | 39.69 | 40.60 | 42.96 |
| $-\Delta_c u^0$/J·g$^{-1}$ | 29341.62 | 29246.46 | 29234.59 | 24623.04 |

$^a$ $\Delta U$ (IBP) already includes the $\Delta U$ (ign) $m$(cpd) is the mass of compound burnt in each experiment; $m'$(fuse) is the mass of fuse (cotton) used in each experiment; $\Delta T_{ad}$ is the corrected temperature rise; $\epsilon_i$ is the energy equivalent of contents in the initial state; $\epsilon_f$ is the energy equivalent of contents in the final state; $\Delta m$(H₂O) is the deviation of mass of water added to the calorimeter from 5222.5 g; $\Delta U$(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U$(fuse) is the energy of combustion of the fuse (cotton); $\Delta U$(HNO₃) is the energy correction for the nitric acid formation; $\Delta U$(As₂O₃)) is the energy correction for the oxidation of the aqueous solution of As₂O₃; $\Delta U$(ign) is the electrical energy for ignition; $\Delta U$((H₂PtCl₆) is the energy correction for the formation of the platinum complex; $\Delta U_\Sigma$ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion.
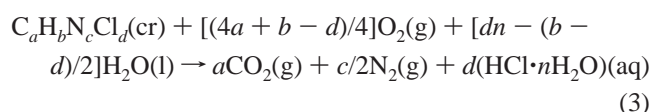
chosen temperature interval of the experiments corresponds to vapor pressures in the range 0.1 to 1.0 Pa.

### 3. Computational Details

The B3LYP method[37,38] together with the 6-31G(d) basis set was used for the optimization of the geometry of all compounds studied here and to calculate the vibrational frequencies. Then, for all minima coming from the previous set of optimization runs, a single-point calculation was performed with a larger basis set, 6-311+G(2d,2p). The vibrational frequencies were also used to extract thermal corrections for $T = 298.15$ K (vibrational, rotational, translational, and pV; a scale factor equal to 0.9804 was used), which were added to the energy of the B3LYP/6-311+G(2d,2p) single-point calculations. The Gaussian 98 package of programs was used throughout this work.[39]

### 4. Results

**4.1. Experimental Thermochemistry.** Detailed results for each combustion experiment performed for each compound are given as Supporting Information. The results for one typical combustion experiment of each compound are reported in Table 1, where $\Delta m$(H₂O) is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\epsilon$ (calor), and $\Delta U_\Sigma$ is the correction to the standard state. The remaining terms are as previously descrived.[30,40] Table 2 lists the individual values of massic energy of combustion together with its mean value, $\langle \Delta_c u^0 \rangle$, and standard deviation. These values of $\Delta_c u^0$ are referred to the combustion reaction described by eq 3

$$C_a H_b N_c Cl_d(cr) + [(4a + b - d)/4]O_2(g) + [dn - (b - d)/2]H_2O(l) \rightarrow aCO_2(g) + c/2N_2(g) + d(HCl \cdot nH_2O)(aq) \tag{3}$$

in which reactants and products are in the thermodynamic standard states, at $T = 298.15$ K, with HCl·600H₂O(aq) as the

**TABLE 2: Individual Values of the Massic Energies of Combustion, $-\Delta_c u^0$, of the Compounds, at $T = 298.15$ K**

| $-\Delta u^0$/J·g$^{-1}$ | | | |
|---|---|---|---|
| 2-Clbzph | 3-Clbzph | 4-Clbzph | 4,4′-Cl₂bzph |
| 29352.38 | 29246.46 | 29220.75 | 24634.09 |
| 29347.17 | 29233.72 | 29234.59 | 24623.04 |
| 29341.62 | 29244.32 | 29237.95 | 24630.06 |
| 29332.97 | 29234.11 | 29235.19 | 24640.95 |
| 29339.50 | 29232.20 | 29243.45 | 24641.08 |
| 29338.32 | 29248.81 | 29246.93 | 24642.96 |
|  |  |  | 24629.39 |
|  |  |  | 24627.65 |
| 29342.0 ± 2.8 | 29239.9 ± 3.0 | 29236.5 ± 3.7 | 24633.6 ± 2.6 |

**TABLE 3: Derived Standard ($p^0 = 0.1$ MP) Molar Energies of Combustion, $\Delta_c U_m^\circ$, Standard Molar Enthalpies of Combustion, $\Delta_c H_m^\circ$, and Standard Molar Enthalpies of Formation, $\Delta_f H_m^\circ$, for the Compounds, at $T = 298.15$ K**

| compound | $-\Delta_c U_m^\circ$(cr)/ kJ·mol$^{-1}$ | $-\Delta_c H_m^\circ$(cr)/ kJ·mol$^{-1}$ | $-\Delta_f H_m^\circ$(cr)/ kJ·mol$^{-1}$ |
|---|---|---|---|
| 2-Clbzph | 6357.4 ± 1.6 | 6361.1 ± 1.6 | 64.4 ± 2.3 |
| 3-Clbzph | 6335.3 ± 1.7 | 6339.0 ± 1.7 | 86.4 ± 2.4 |
| 4-Clbzph | 6334.6 ± 2.0 | 6338.3 ± 2.0 | 87.2 ± 2.6 |
| 4,4′-Cl2bzph | 6185.8 ± 1.7 | 6188.3 ± 1.7 | 117.9 ± 2.4 |

chlorine-containing product in the final state. Table 3 lists the derived standard molar energies and enthalpies of combustion and standard molar enthalpies of formation for the studied compounds in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical practice,[41,42] 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 auxiliary quantities used. To derive $\Delta_f H_m^\circ$(cr) from $\Delta_c H_m^\circ$(cr) the standard molar enthalpies of formation of CO₂(g), −393.51 ± 0.13 kJ·mol$^{-1}$;[43] H₂O(l), −285.830 ± 0.042 kJ·mol$^{-1}$,[43] and HCl in 600 H₂O(l), −166.540 ± 0.005 kJ·mol$^{-1}$,[26,43] were used.

Five independent measurements of the enthalpy of sublimation of 2-Clbzph, at $T = 401$ K, by microcalorimetry, yielded the average value of $\Delta_{cr,298.15K}^{g,T} H_m = 122.8 \pm 0.4$ kJ·mol$^{-1}$, with the respective uncertainty, taken as twice the standard deviations of the mean. The standard molar enthalpy of phase transition, at $T = 298.15$ K, was calculated $\Delta_{cr}^g H_m^\circ$ ($T = 298.15K) = 100.2 \pm 0.4$ kJ·mol$^{-1}$ by means of eq 4

$$\Delta_{cr}^g H_m^\circ(T = 298.15 \text{ K}) = \Delta_{cr,298.15K}^{g,T} H_m - \Delta_{298.15K}^T H_m^\circ(g) \tag{4}$$

using $\Delta_{298.15K}^T H_m^\circ(g) = 22.6$ kJ·mol$^{-1}$ estimated by a group-additivity method (i.e., 2-Clbzph = chlorobenzene + benzene + acetone-2-methane), based on the values of Stull et al.[34]

The integrated form of the Clausius-Clapeyron equation, ln-$(p/Pa) = a - b (T/K)^{-1}$, where $a$ is a constant and $b = \Delta_{cr}^g H_m^\circ(\langle T \rangle)/R$, was used to derive the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range. The experimental results obtained from each effusion cell, together with the residuals of the Clausius−Clapeyron equation, derived from least-squares adjustment is presented in Table 4. For each substance, the calculated enthalpies of sublimation obtained from each individual hole are in good agreement within experimental uncertainty. The entropies of sublimation, at equilibrium conditions, were calculated as

$$\Delta_{cr}^g S_m\{\langle T \rangle, p(T = \langle T \rangle)\} = \Delta_{cr}^g H_m^\circ(\langle T \rangle)/\langle T \rangle \tag{5}$$

**TABLE 4: Knudsen-Effusion Results for 3-Clbzph, 4-Clbzph, and 4,4′-Cl₂bzph[a]**

| T/K | p/Pa | | | 10²Δln (p/Pa) | | |
|---|---|---|---|---|---|---|
| | hole 1 | Hole 2 | hole 3 | hole 1 | hole 2 | hole 3 |
| | | 3-Chlorobenzophenone | | | | |
| 321.114 | 0.121 | 0.121 | 0.121 | 1.2 | 0.9 | 0.0 |
| 323.289 | 0.161 | 0.159 | 0.158 | 0.4 | 1.0 | 1.2 |
| 325.284 | 0.209 | 0.210 | 0.204 | −0.9 | −2.2 | 0.1 |
| 327.116 | 0.256 | 0.255 | 0.261 | 1.1 | 1.2 | −1.9 |
| 329.267 | 0.342 | 0.332 | 0.332 | −1.8 | 0.9 | 0.3 |
| 331.278 | 0.431 | 0.435 | 0.425 | −0.4 | −2.0 | −0.3 |
| 333.283 | 0.547 | 0.553 | 0.537 | −0.6 | −2.3 | −0.1 |
| 335.262 | 0.695 | 0.677 | 0.674 | −1.5 | 0.6 | 0.4 |
| 337.112 | 0.841 | 0.835 | 0.838 | 0.9 | 1.0 | 0.1 |
| 339.112 | 1.049 | 1.050 | 1.053 | 1.7 | 1.0 | 0.1 |
| | | 4-Chlorobenzophenone | | | | |
| 320.099 | 0.133 | 0.135 | 0.138 | 2.2 | 0.3 | −0.5 |
| 322.290 | 0.182 | 0.177 | 0.182 | −1.8 | −0.2 | −1.3 |
| 324.272 | 0.228 | 0.224 | 0.224 | −0.4 | 0.7 | 1.8 |
| 326.141 | 0.283 | 0.285 | 0.283 | 0.6 | −0.7 | 0.4 |
| 328.286 | 0.373 | 0.366 | 0.368 | −1.6 | −0.5 | −0.8 |
| 330.227 | 0.461 | 0.456 | 0.451 | 0.1 | 0.4 | 1.5 |
| 332.121 | 0.573 | 0.572 | 0.570 | 0.3 | −0.1 | −0.3 |
| 334.283 | 0.737 | 0.734 | 0.730 | −0.1 | −0.3 | −0.5 |
| 336.215 | 0.919 | 0.908 | 0.898 | −0.2 | 0.3 | 0.3 |
| 338.118 | 1.125 | 1.126 | 1.118 | 0.9 | 0.1 | −0.5 |
| | | 4,4′-Dichlorobenzophenone | | | | |
| 349.286 | 0.157 | 0.155 | 0.158 | −0.8 | 0.3 | −1.2 |
| 351.249 | 0.194 | 0.194 | 0.192 | 0.1 | −0.2 | 1.2 |
| 353.139 | 0.236 | 0.240 | 0.237 | 1.4 | −0.4 | 0.7 |
| 355.276 | 0.304 | 0.302 | 0.307 | −0.4 | 0.2 | −1.8 |
| 357.238 | 0.375 | 0.375 | 0.367 | 0.0 | −0.1 | 1.7 |
| 359.128 | 0.455 | 0.456 | 0.455 | 1.1 | 0.6 | 0.3 |
| 361.279 | 0.588 | 0.578 | 0.578 | −1.6 | −0.2 | −0.8 |
| 363.236 | 0.714 | 0.712 | 0.702 | −0.4 | −0.6 | 0.3 |
| 365.134 | 0.863 | 0.862 | 0.858 | 0.5 | 0.0 | −0.2 |
| 365.279 | 0.886 | 0.874 | 0.879 | −0.7 | 0.1 | −1.1 |
| 367.241 | 1.069 | 1.067 | 1.053 | 0.8 | 0.3 | 0.9 |

[a] The equilibrium vapor-pressure is denoted by p, and the deviations of experimental results from those given by the Clausius−Clapeyron equation are denoted by Δln (p/Pa).
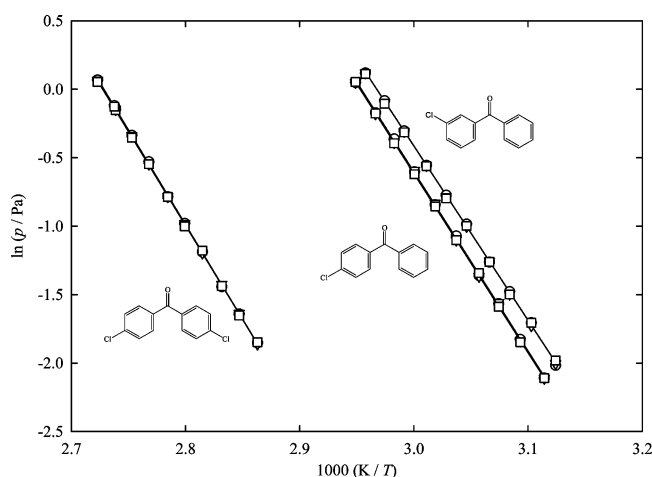


**Figure 1.** Plots of ln(p/Pa) against 1/T for 3-Clbzph, 4-Cl₂bzph and 4,4′-Cl₂bzph. ○, smaller holes; ▽, medium holes; and; □, larger holes.[3]

Detailed parameters of the Clausius−Clapeyron equation, together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature, $T = \langle T \rangle$, are presented in Table 5. These data is presented for each hole used and for the global treatment of all of the (p, T) points obtained for each studied compound. The plots of ln $p = f(1/T)$ for the global results of the three crystalline compounds studied are presented in Figure 1, whereas in Table 6 are reported the

(p,T) values for the same three compounds calculated from the (p,T) equations within the experimental range of pressures used: 0.1−1 Pa. Sublimation enthalpies, at the temperature 298.15 K, were derived from the sublimation enthalpies calculated at the mean temperature $\langle T \rangle$ of the experiments, by use of the equation

$$\Delta_{cr}^{g} H_m^{\circ}(T = 298.15K) = \Delta_{cr}^{g} H_m^{\circ}(\langle T \rangle) + \Delta_{cr}^{g} c_{p,m}^{\circ}(298.15K - \langle T \rangle) \quad (6)$$

Values of $\Delta_{cr}^{g} c_{p,m}^{\circ}$ were estimated for each compound $\Delta_{cr}^{g} c_{p,m}^{\circ} = -50$ J·K⁻¹·mol⁻¹, in accordance with similar estimations made by other authors.[44] Table 7 presents for each compound the values of the standard molar enthalpies at $T = 298.15$ K and the entropies and Gibbs energies of sublimation. The combination of the standard molar enthalpies of formation in the crystalline state given in Table 3, with the standard molar enthalpies of sublimation, given in Table 7, yield the standard molar enthalpies of formation of the studied chlorobenzophenones, in the gaseous state (at $T = 298.15$ K), which are summarized in Table 8. The results obtained for the three monochlorobenzophenones show clearly that 2-Clbzph is rather unstable when compared with the other two isomers which are almost degenerate. This suggests that stabilizing intramolecular H···Cl hydrogen bonds possible in the case of 2-Clbzph are not important. Further, the small enthalpy of sublimation determined for this compound shows also that intermolecular H···Cl hydrogen bonds are also absent or weaker than those in 3-Clbzph and 4-Clbzph.

**4.2. Computational Thermochemistry.** The most stable configurations for all of the mono- and dichlorobenzophenones are shown in Figure 2. Selected geometrical parameters are also included in that figure and show that, in general, there are not significant differences between the geometry of benzophenone and of the halogenated derivatives. For example, the largest C= O bond length is 1.227 Å, in the cases of benzophenone and 4-Clbzph, whereas the shortest C=O bond length is calculated for 2,6-Cl₂bzph; the difference between the largest and shortest bonds is only 0.009 Å. These geometrical parameters suggest that the insertion of chlorine atoms into the rings of benzophenone exerts a small effect on the carbonyl bond. This suggests also that the carbonyl group has the ability to attenuate electron density differences due to the positioning of chlorine atoms attached to the benzophenone rings. The role of the C=O bond detected here is similar to the role of the carbonyl bond in 2-benzoyl-3-methylquinoxaline-1,4-dioxide and 2-tert-butoxy-carbonyl-3-methylquinoxaline-1,4-dioxide for which identical N−O bond dissociation enthalpies have been calculated, even despite different kinds of effects (mesomeric or inductive) are associated with the groups substituted at the position 2 of the quinoxaline ring.[45] Larger differences between the shortest and the longest bonds are found for the C−C and C−Cl bonds respectively of 0.029 and 0.019 Å. The C−C−C angles are 120.7° in the case of the unsubstituted benzophenone compound, 120.0° in 2,3-Cl₂bzph and 122.9° in the case of 2,2′-Cl₂bzph The only structural parameter that changes drastically is that used to define the rotation of the rings with respect to the C= O bond. The comparison between the two rings is possible if one considers the C1−C2-C3−C4 dihedral angle with higher values meaning a much more twisted structure. In the case of benzophenone, this angle is 50.0°, and identical angles are calculated for the compounds without chlorine substitution in position 2, suggesting again that the chlorine atoms do not introduce significant electronic effects in the halogenated

Molecular Energetics of Chlorobenzophenones

*J. Phys. Chem. B, Vol. 111, No. 45, 2007* **13037**

**TABLE 5: Experimental Results for 3-Clbzph, 4-Clbzph, and 4,4′-Cl₂bzph where *a* and *b* are from Clausius−Clapeyron Equation ln (p/Pa) = *a* − *b*·(K/T), and *b* = $\Delta_{cr}^{g}H_m^\circ(\langle T\rangle)/R$; R = 8.31451 J·K⁻¹·mol⁻¹**

| orifice number | *a* | *b* | $\langle T\rangle$/K | $p(\langle T\rangle)$/Pa | $\Delta_{cr}^{g}H_m^\circ(\langle T\rangle)/$ kJ·mol⁻¹ | $(\Delta_{cr}^{g}S_m\{\langle T\rangle, p(T=\langle T\rangle)\})/$ J·K⁻¹·mol⁻¹ |
|---|---|---|---|---|---|---|
| | | | 3-Chlorobenzophenone | | | |
| 1 | 38.67 ± 0.23 | 13090 ± 77 | | | 108.8 ± 0.6 | |
| 2 | 38.64 ± 0.29 | 13082 ± 97 | | | 108.8 ± 0.8 | |
| 3 | 38.64 ± 0.15 | 13086 ± 50 | | | 108.8 ± 0.4 | |
| global results | 38.65 ± 0.13 | 13086 ± 44 | 330.11 | 0.371 | 108.8 ± 0.4 | 329.6 ± 1.2 |
| | | | 4-Chlorobenzophenone | | | |
| 1 | 37.80 ± 0.22 | 12739 ± 74 | | | 105.9 ± 0.6 | |
| 2 | 37.82 ± 0.09 | 12747 ± 29 | | | 106.0 ± 0.2 | |
| 3 | 37.26 ± 0.19 | 12564 ± 63 | | | 104.5 ± 0.5 | |
| global results | 37.63 ± 0.11 | 12683 ± 37 | 329.11 | 0.404 | 105.4 ± 0.3 | 320.3 ± 0.9 |
| | | | 4,4′-Dichlorobenzophenone | | | |
| 1 | 37.73 ± 0.17 | 13828 ± 62 | | | 115.0 ± 0.5 | |
| 2 | 37.57 ± 0.07 | 13772 ± 25 | | | 114.5 ± 0.2 | |
| 3 | 37.43 ± 0.22 | 13724 ± 78 | | | 114.1 ± 0.6 | |
| global results | 37.58 ± 0.10 | 13775 ± 34 | 358.26 | 0.419 | 114.5 ± 0.3 | 328.0 ± 0.8 |

**TABLE 6: p/T Values from the Vapor-Pressure Equations for 3-Clbzph, 4-Clbzph, and 4,4′-Cl₂bzph**

| p/Pa | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | T/K | | | | | |
| 3-Clbzph | 319.5 | 325.0 | 328.3 | 330.7 | 332.6 | 334.2 | 335.5 | 336.6 | 337.7 | 338.6 |
| 4-Clbzph | 317.6 | 323.2 | 326.6 | 329.0 | 330.9 | 332.5 | 333.9 | 335.1 | 336.1 | 337.0 |
| 4,4′-Cl₂bzph | 345.4 | 351.5 | 355.2 | 357.8 | 359.9 | 361.6 | 363.1 | 364.4 | 365.5 | 366.6 |

**TABLE 7: Values of the Standard (p° = 0.1 MPa) Molar Enthalpies, $\Delta_{cr}^{g}H_m^\circ$, Entropies, $\Delta_{cr}^{g}S_m^\circ$, and Gibbs Energies, $\Delta_{cr}^{g}G_m^\circ$, of Sublimation, at T = 298.15 K, for the Four Chlorobenzophenones Experimentally Studied**

| compound | $\Delta_{cr}^{g}H_m^\circ/$ kJ·mol⁻¹ | $\Delta_{cr}^{g}S_m^\circ/$ J·K⁻¹·mol⁻¹ | $\Delta_{cr}^{g}G_m^\circ/$ kJ·mol⁻¹ |
|---|---|---|---|
| 2-Clbzph | 100.2 ± 0.4 | | |
| 3-Clbzph | 110.4 ± 0.4 | 230.7 ± 1.2 | 41.6 ± 0.5 |
| 4-Clbzph | 108.2 ± 0.3 | 222.0 ± 0.9 | 42.0 ± 0.4 |
| 4,4′-Cl2bzph | 117.5 ± 0.3 | 234.2 ± 0.8 | 47.7 ± 0.4 |

**TABLE 8: Derived Standard (p⁰ = 0.1 MPa) Molar Enthalpies of Formation $\Delta_f H_m^\circ$ at T = 298.15 K**

| compound | $-\Delta_f H_m^\circ(cr)/$ kJ·mol⁻¹ | $\Delta_{cr}^{g}H_m^\circ/$ kJ·mol⁻¹ | $\Delta_f H_m^\circ(g)/$ kJ·mol⁻¹ |
|---|---|---|---|
| 2-Clbzph | 64.4 ± 2.3 | 100.2 ± 0.4 | 35.6 ± 2.3 |
| 3-Clbzph | 86.4 ± 2.4 | 110.4 ± 0.4 | 24.0 ± 2.4 |
| 4-Clbzph | 87.2 ± 2.6 | 108.2 ± 0.3 | 21.0 ± 2.6 |
| 4,4′-Cl2bzph | 117.9 ± 2.4 | 117.5 ± 0.3 | −0.4 ± 2.4 |

molecules when compared with the parent compound. However, in the cases where single or double substitution occurs at the carbon atoms adjacent to the carbonyl group, the C1−C2-C3−C4 dihedral angle increases dramatically to 74.7° in the case of 2,6-Cl₂bzph showing a strong steric interaction between Cl atoms and the opposite rings. In fact, this is an interesting example since the plane of the ring with two chlorine atoms is normal to the plane that contains the C=O bond. Additional information is also extracted from the comparison of the intramolecular H···H, H···Cl, or Cl···Cl distances also displayed in Figure 2 which have the largest values in the case of 2,2′-Cl₂bzph and 2,6-Cl₂bzph even the ordering is changed with respect to the C1−C2-C3−C4 dihedral angle.

The structures optimized at the B3LYP/6-31G(d) level of theory for 2-Clbzph and 2,5-Cl₂bzph may be compared with the experimental X-ray diffraction crystal structures determined by Pinkus et al.[46] Despite the fact that gas-phase structures are compared with crystalline ones, the geometrical differences are small and, more importantly, the orientation of the chlorine atoms with respect to the C=O group is also maintained in the

crystals, i.e., the chlorine atoms prefer to be the farthest possible from the carbonyl group. Also interesting, the rotation of the rings is larger in the case of the solids, suggesting that internal H···Cl hydrogen bonds are very weak. In fact, in the case of gas-phase 2-Clbzph, the conformation shown in Figure 2 is only 2.5 kJ·mol⁻¹ more stable than the conformer with the chlorine atom in the opposite side of the ring, i.e., closer to the carbonyl group. The calculated B3LYP/6-311+G(2d,2p)//B3LYP/6-31G-(d) enthalpies of the several stable different configurations studied theoretically for the mono and dichlorobenzophenones are given as Supporting Information.

The enthalpies of formation of the three different monochlorobenzophenones and of the twelve dichlorobenzophenones were calculated by using one of the following working reactions

chlorobenzophenone + benzene → benzophenone + chlorobenzene (7)

dichlorobenzophenone + benzene → benzophenone + 1,2-dichlorobenzene (8)

dichlorobenzophenone + benzene → benzophenone + 1,3-dichlorobenzene (9)

dichlorobenzophenone + benzene → benzophenone + 1,4-dichlorobenzene (10)

dichlorobenzophenone + 2 benzene → benzophenone + 2 chlorobenzene (11)
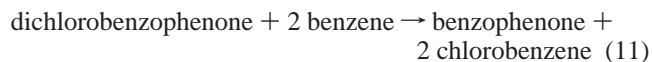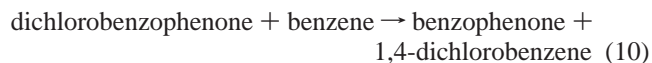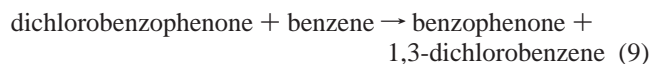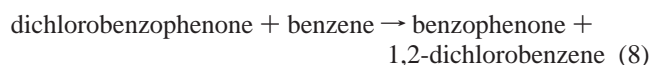
and the experimental enthalpies of formation for benzene, $\Delta_f H_m^\circ(g) = 82.6 \pm 0.7$ kJ·mol⁻¹,[47] benzophenone, 49.9 ± 3.0 kJ·mol⁻¹,[48] chlorobenzene, 52.0 ± 1.3 kJ·mol⁻¹,[47] 1,2-dichlorobenzene, 30.2 ± 2.1 kJ·mol⁻¹,[47] 1,3-dichlorobenzene, 25.7 ± 2.1 kJ·mol⁻¹,[47] and 1,4-dichlorobenzene, 22.5 ± 1.5 kJ·mol⁻¹.[47] Reaction 7 has been used to estimate the standard gas-phase enthalpies of formation of the monochlorobenzophenones and reaction 11 the enthalpies of formation of the dichlorobenzophenones with a chlorine atom in each ring. Reaction 8 has been used to estimate the enthalpy of formation of 2,3-Cl₂bzph and 3,4-Cl₂bzph. This suggests also that the carbonyl has been
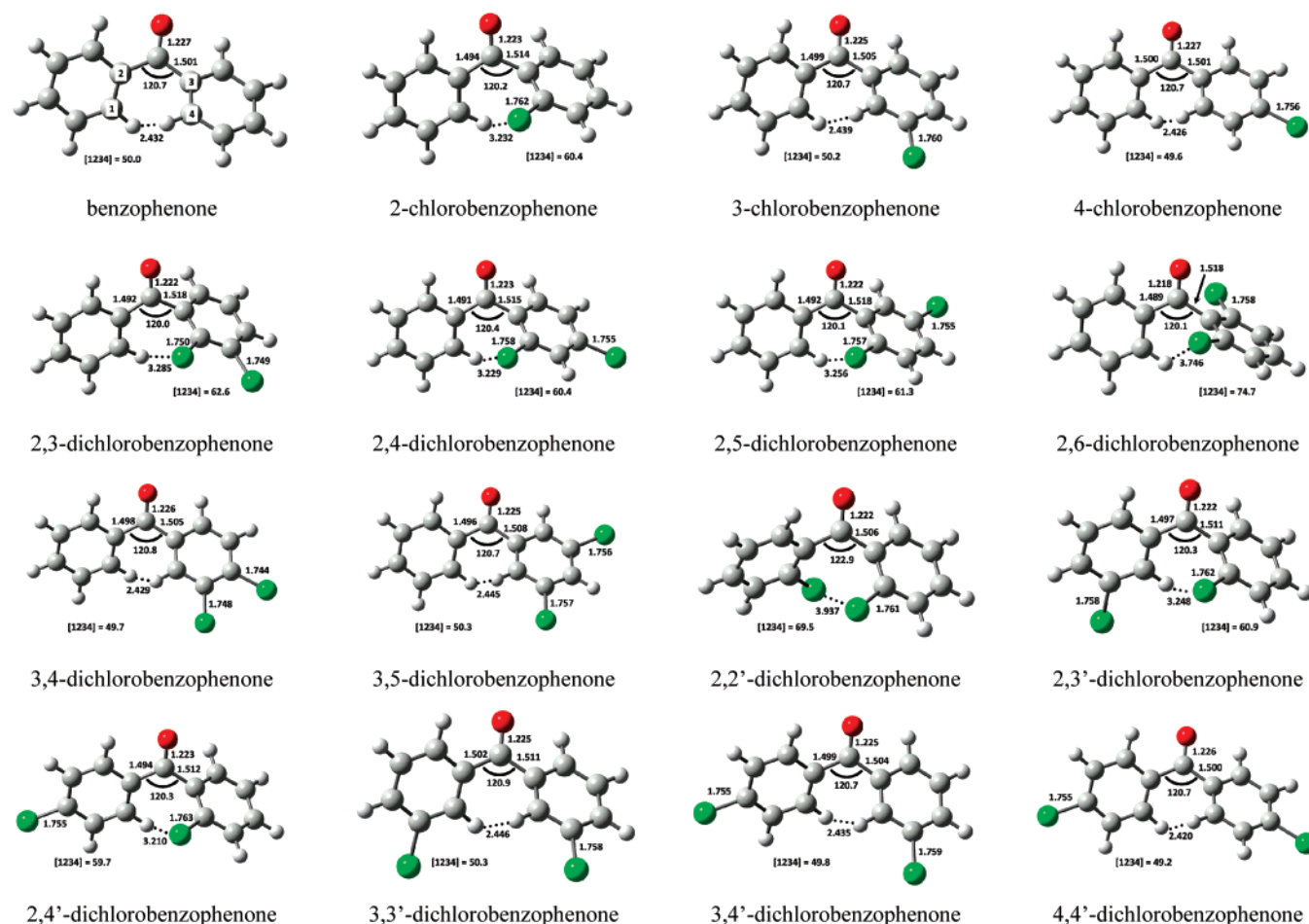
**Figure 2.** Optimized most stable configurations for the mono- and dichlorobenzophenones. Selected distances are in Å and angles in degrees.

**TABLE 9: Computed Enthalpies of the Working Reactions ($\Delta H_R$) Used to Calculate the Enthalpies of Formation ($\Delta H_f$) of the Three Monochlorobenzophenones and 12 Dichlorobenzophenones[a]**

| compound | reaction | $\Delta H_R$ | $\Delta H_f$ | $\Delta\Delta H$ |
|---|---|---|---|---|
| 2-Clbzph | 7 | −15.2 | 34.5 | 1.1 |
| 3-Clbzph | 7 | −2.5 | 21.8 | 2.2 |
| 4-Clbzph | 7 | −0.5 | 19.8 | 1.2 |
| 2,3-Cl₂bzph | 8 | −16.7 | 14.2 | |
| 2,4-Cl₂bzph | 9 | −16.4 | 9.4 | |
| 2,5-Cl₂bzph | 10 | −15.0 | 5.4 | |
| 2,6-Cl₂bzph | 9 | −22.6 | 15.6 | |
| 3,4-Cl₂bzph | 8 | −2.3 | −0.2 | |
| 3,5-Cl₂bzph | 9 | −4.7 | −2.3 | |
| 2,2′-Cl₂bzph | 11 | −35.4 | 24.1 | |
| 2,3′-Cl₂bzph | 11 | −18.1 | 6.8 | |
| 2,4′-Cl₂bzph | 11 | −15.7 | 4.4 | |
| 3,3′-Cl₂bzph | 11 | −5.9 | −5.4 | |
| 3,4′-Cl₂bzph | 11 | −3.6 | −7.7 | |
| 4,4′-Cl₂bzph | 11 | −1.8 | −9.6 | 9.2 |

[a] $\Delta\Delta H$ is the difference between the experimental and the calculated enthalpies of formation. All values are in kJ·mol⁻¹.

used for 2,4-Cl₂bzph, 2,6-Cl₂bzph and 3,5-Cl₂bzph species, and, finally, reaction 10 has been used to estimate the $\Delta_f H_m^\circ(g)$ of the 2,5-Cl₂bzph isomer. The full set of estimated enthalpies of formation is reported in Table 9. Starting with the monochlorobenzophenones, the estimated enthalpies of formation are in excellent agreement with the experimental ones. The differences between experimental and B3LYP estimated $\Delta_f H_m^\circ(g)$ are smaller than the uncertainties associated with the experimental results. The excellent agreement between experimental and computed values support the conclusions obtained from the

analysis of geometrical data; that is, the insertion of chlorine atoms does not significantly influence the molecule and the atomic neighborhoods are similar on both sides of reaction 1. The much more positive enthalpy of formation found for 2-Clbzph when compared with the other two monochlorobenzophenones, for which identical values are observed, show also that the energetics of these compounds are mainly governed by the presence (2-Clbzph) or absence (3- and 4-Clbzph) of the destabilizing steric interaction between Cl and the opposite phenyl ring, as also suggested by the higher C1−C2-C3−C4 dihedral angle calculated for the former compound.

The insertion of chlorine atoms into the parent benzophenone compounds yielding the different dichlorobenzophenones may be performed in two different ways, i.e., with the chlorine atoms entering (i) the same ring or (ii) different rings. In the case of option i, the calculations suggest that 3,5-Cl₂bzph is the most stable isomer and that the 2,6-Cl₂bzph compound is the least stable one. Interestingly, the comparison of the enthalpies of formation of 2,3-Cl₂bzph and of 2,6-Cl₂bzph with those of 3,4-Cl₂bzph and 3,5-Cl₂bzph suggests that the unstable Cl•••••C═O interactions are less important in 2,6-Cl₂bzph than in 2-Clbzph. In fact, the difference between the enthalpies of formation of 3,4-Cl₂bzph and 3,5-Cl₂bzph is of only 2.1 kJ·mol⁻¹ which is identical to the 1.4 kJ·mol⁻¹ difference between 2,3-Cl₂bzph and of 2,6-Cl₂bzph, i.e., the instability due to two Cl•••C═O interactions is similar to that caused by the combination of a Cl•••C═O interaction and a Cl•••Cl interaction. In the case of chlorine substitution into two different rings, the calculations predict that the 4,4′-Cl₂bzph isomer is the most stable of the benzophenones with a chlorine atom per ring and

Molecular Energetics of Chlorobenzophenones

*J. Phys. Chem. B, Vol. 111, No. 45, 2007* **13039**

that is also the most stable of the dichlorobenzophenones. Its estimated enthalpy of formation is $-9.6$ kJ·mol$^{-1}$ a value that differs by 9.2 kJ·mol$^{-1}$ from the experimental result determined in the present work. Since there is only an experimental result for comparison purposes, it is rather difficult to check the consistency of the B3LYP approach, together with reaction 11, for the estimation of enthalpies of formation of doubly chlorine substituted benzophenones. Nevertheless, the enthalpic difference between the experimental and calculated result for 4,4′-Cl$_2$bzph is acceptable since the observed difference is only the double of the desired accuracy wanted for other computational thermochemistry approaches that are much more CPU demanding. Importantly, the ordering of the estimated enthalpies of formation for benzophenones containing a chlorine atom per ring are in perfect agreement with the experimentally determined enthalpies.

## 5. Conclusions

A combined experimental and theoretical study was performed and the standard molar enthalpies of formation in the gas-phase of all mono- and dichlorobenzophenones have been obtained. In the case of the three monochlorobenzophenones, it is shown that the 2-chlorobenzophenone is rather unstable when compared with the other two isomers. This suggests that intramolecular H···Cl hydrogen bonds are not critical. Furthermore, the enthalpies of sublimation determined experimentally for the monochlorobenzophenones show that intermolecular H···Cl hydrogen bonds are much weaker in the case of 2-chlorobenzophenones than in the other two possible singly chlorinated isomers. The experimental results are in excellent agreement with the results calculated using the B3LYP approach.

In the case of the doubly chlorinated compounds, only 4,4′-dichlorobenzophenone was studied experimentally. Its determined enthalpy of formation differs by $\sim 9$ kJ·mol$^{-1}$ from the estimated DFT based result. Even though this is not a very large difference, one should use these values with some caution. The 4,4′-Cl$_2$bzph isomer is predicted to be the most stable of the benzophenones. Consideration of all of the calculated enthalpies of formation suggests that 3,5-Cl$_2$bzph is the most stable dichloro isomer with two chlorine atoms bonded to the same ring, whereas the 2,6-Cl$_2$bzph compound is the least stable one. It is also shown that unstable Cl···C=O interactions are less important in 2,6-Cl$_2$bzph than in 2-Clbzph.

**Supporting Information Available:** Detailed data of the effusion orifices (diameter and Clausing factors) of the Knudsen effusion apparatus, details of all the combustion calorimetry experiments of each of the four compounds studied experimentally and computed enthalpies for all the mono and dichlorobenzophenones. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) McDonough, J. A.; Durrwachter, J. R. *Org. Process Res. Dev.* **1997**, *1*, 268.

(2) Gates, M. *J. Org. Chem.* **1980**, *45*, 1675.

(3) Bachmann, W. E.; Carlson, E.; Moran, J. C. *J. Org. Chem.* **1948**, *13*, 916.

(4) Hu, B.; Mosher, H. S. *J. Org. Chem.* **1986**, *51*, 1904.

(5) Ribeiro da Silva, M. A. V.; Ferrão M. L. C. H.; Jiye, F. *J. Chem. Thermodyn.* **1994**, *6*, 839−846.

(6) Morais, V. M. F.; Miranda, M. S.; Matos, M. A. R. *J. Chem. Eng. Data* **2007**, *52*, 627−634.

(7) Ribeiro da Silva, M. A. V.; Ferreira, A. I. M. C. L.; Gomes, J. R. B. *J. Phys. Chem. B* **2005**, *109*, 13356−13362.

(8) Ribeiro da Silva, M. A. V.; Lima, L. M. S. S.; Amaral, L. M. P. F.; Ferreira, A. I. M. C. L.; Gomes, J. R. B. *J. Chem. Thermodyn.* **2003**, *35*, 1343−1359.

(9) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Gomes, J. R. B. *J. Phys. Chem. A* **2006**, *110*, 9301−9306.

(10) Ribeiro da Silva, M. A. V.; Ferreira, A. I. M. C. L.; Amaral, L. M. P. F. *J. Chem. Thermodyn.* **2002**, *34*, 119−127.

(11) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Gomes, J. R. B. *Pol. J. Chem.* **2007**, *81*, 865−873.

(12) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Matos, M. A. R. *J. Chem. Thermodyn.* **1997**, *29*, 1535−1543.

(13) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Gomes, J. R. B. *Chem. Phys. Lett.* **2005**, *406*, 154−160.

(14) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Alves da Silva, A. M. R. O. *J. Chem. Thermodyn.* **1995**, *27*, 633−641.

(15) Morais, V. M.; Miranda, M. S.; Matos, M. A. R. *J. Chem. Thermodyn.* **2004**, *36*, 377−383.

(16) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Gomes, J. R. B. *J. Phys. Chem. B* **2007**, *111*, 792−799.

(17) Ribeiro da Silva, M. A. V.; Amaral, L. M. P. F.; Matos, M. A. R. *J. Chem. Thermodyn.* **2006**, *38*, 49−55.

(18) Sunner, S. In *Experimental Chemical Thermodynamic*s; Sunner, S., Månsson, M., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, Chapter 2.

(19) Vale, M. L. C. *Graduation Thesis*, Faculty of Science, University of Porto, 1989.

(20) Silva, A. M. R. O. A. *M.Sc. Thesis*, Faculty of Science, University of Porto, 1993.

(21) Santos, L. M. N. F. *Ph.D. Thesis*, University of Porto, 1995.

(22) Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, *60*, 1080−1089.

(23) Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodyn.* **1972**, *4*, 283−299.

(24) Sunner, S.; Thorén, S. *Acta Chem. Scand.* **1964**, *18*, 1528−1532.

(25) Sellers, P.; Sunner, S.; Wadsö, I. *Acta Chem. Scand.* **1964**, *18*, 202−206.

(26) The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data* **1982**, 11 (Suppl. 2).

(27) Coops, J.; Jessup, R. S.; Van Nes, K. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 3.

(28) Vogel, A. I. *Quantitative Inorganic Analysis*; Longmans: London, 1978.

(29) Washburn, E. W. *J. Rest. Bur. Stand. (U.S.)* **1933**, *10*, 525−588.

(30) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(31) Wieser, M. E. *Pure Appl. Chem.* **2006**, *78*, 2051−2066.

(32) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221−228.

(33) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V. *Thermochim. Acta* **2004**, *415*, 15−20.

(34) Stull, D. R.; Westrum, Jr., E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(35) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Planas Leitão, M. L.; Roux, M. V.; Torres, L. A. *Thermochim. Acta* **1999**, *331*, 93.

(36) Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Santos, L. M. N. B. *J. Chem. Thermodyn.* **2006**, *38*, 778−787.

(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1980**, *37*, 785.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(40) Bjellerup, L. G. In *Experimental Thermochemistry*; Skinner, H. A., Ed.; Interscience: New York, 1962; Vol. 2, Chapter 3.

(41) Rossini, F. D. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 14.

(42) Olofsson, G. In *Combustion Calorimetry*; Sunner, S., Månsson, M., Eds.; Pergamon Press: Oxford, 1979; Chapter 6.

(43) Cox, J. D., Wagman, D. D., Medvedev, A., Eds.; *CODATA Key values for Thermodynamics*; Hemisphere: New York, 1989.

(44) Burkinshaw, P. M.; Mortimer, C. T. *J. Chem. Soc. Dalton Tran*s. **1984**, 75−77.

(45) Gomes, J. R. B.; Sousa, E. A.; Gonçalves, J. M.; Gales, L.; Damas, A. M.; Gomes, P.; Pandey, S.; Acree, W. E., Jr.; Ribeiro da Silva, M. D. M. C. *J. Phys. Org. Chem.* **2007**, *20*, 491−498.

(46) Pinkus, A. G.; Klausmeyer. K. K.; Feazell, R. P.; Meng, L. Y. C.; Chang, T. C. *J. Chem. Crystallogr.* **2004**, 637−640.

(47) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Centre: College Station, TX, 1994.

(48) Sabbah, R.; Laffitte, M. *Thermochim. Acta* **1978**, *23*, 196−198.