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Experimental and Computational Studies on the Structural and Thermodynamic Properties of Two Sulfur Heterocyclic Keto Compounds

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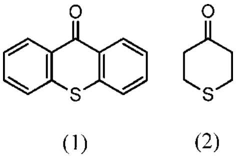
The present work reports the standard ($p° = 0.1$ MPa) molar enthalpies of formation in the gaseous phase of thioxanthone, (91.9 ± 2.4) $\mathrm{kJ \cdot mol^{-1}}$, and tetrahydrothio-$\gamma$-pyrone, ($-164.6 \pm 2.0$) $\mathrm{kJ \cdot mol^{-1}}$, at $T = 298.15$ K, derived from their standard molar energies of combustion and standard molar enthalpies of sublimation, measured by rotating-bomb combustion calorimetry and by the vacuum drop microcalorimetric technique, respectively. For comparison purposes, we performed additional standard ab initio molecular orbital calculations, using the G3(MP2)//B3LYP composite procedure, which were used for the calculation of the enthalpies of several homodesmotic reactions, allowing us to extract the standard molar enthalpies of formation, in the gaseous phase, of the two heterocycles considered in this work. The calculated results are in excellent agreement with the experimental data. The three-dimensional structure of the crystal tetrahydrothio-γ-pyrone was also determined by X-ray crystallography.

Introduction

Heteropolycyclic compounds, constituted from two benzenic rings fused to a central heteroatomic hexagonal ring (containing oxygen or sulfur) like xanthene and thioxanthene and their derivatives, have found a wide range of applicability in several areas. These compounds have an interesting structure/scaffold and a biological efficacy, motivating many scientists to synthesize new derivatives for the development of potential new drug candidates and also for other applications. The information available in the literature regarding the thermodynamic properties for this class of compounds is scarce. As referred to in previous works,[1−3] the problems are even more dramatic since, even for such a small number of results, there are some conflicts caused by significant differences between data for the same compound. These facts prompted us to continue the determination of thermochemical data for a larger number of heteropolycyclic compounds. Thioxanthone (9*H*-thioxanthen-9-one) (Scheme 1) structurally has the core of thioxanthene with a ketone functional group in position 9. This compound and its derivatives, due to the chemical nature and position of the substituent in the aromatic ring, have an important role in many photochemical processes. In fact, they are efficient photosensitizers, which have attracted much attention in recent years owing to their broad spectrum of antitumor activities and great potential to be developed as novel antitumor agents[4] and promising photoinitiators due to their absorption characteristics at near UV range.[5] The molecular structure of the monocyclic compound, tetrahydrothio-γ-pyrone (tetrahydro-4*H*-thiopyran-4-one) (Scheme 1), presents a similar molecular environment of the central ring thioxanthone.

Scheme 1. Molecular Structures of Thioxanthone (1) and Tetrahydrothio-γ-pyrone (2)



In the present work, rotating-bomb calorimetry and the Calvet microcalorimetry techniques were used for the determination of the enthalpies of formation in the crystalline phase and of the solid-to-gas transition, respectively, of the sulfur heterocyclic compounds. From the standard molar enthalpies of formation in the crystalline state, $\Delta_f H_m^o(\mathrm{cr})$, and from the standard molar enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^o$, both at $T = 298.15$ K, the standard molar enthalpies of formation in the gaseous phase, $\Delta_f H_m^o(\mathrm{g})$, at $T = 298.15$ K, were derived. Additionally, the crystal structure of tetrahydrothio-γ-pyrone was determined by X-ray diffraction, and composite calculations with the G3(MP2)//B3LYP approach were performed allowing direct comparison of the experimental data with the optimized structures and the enthalpies of formation computed with appropriate working reactions.

Experimental Section

Purification of the Compounds. In the calorimetric studies, it is a precondition that all the samples of compounds subjected to the measurements have to present high purity (mass fraction higher than 0.99). For this reason, most of the compounds have to be purified before the calorimetric measurements.

The compounds thioxanthone [CAS 492-22-8] and tetrahydrothio-γ-pyrone [CAS 1072-72-6] were purchased from Ald-

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rich Chemical Co., with the, respectively, average mass of fraction 0.97 and 0.99, according to the specifications. Thioxanthone was recrystallized two times from methanol and then sublimated under reduced pressure. Tetrahydrothio-γ-pyrone was purified by repeated sublimation under reduced pressure at room temperature. The purities of the final samples were checked by gas chromatography, using an Agilent 4890 apparatus equipped with an HP-5 column, cross-linked, 5 % diphenyl and 95 % dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness), using acetone as solvent in the analysis, confirming a purity of 99.93 % for thioxanthone and 99.99 % for tetrahydrothio-γ-pyrone.

Other Materials. The compounds used in calibrations of the calorimetric systems were: benzoic acid [CAS 65-85-0], Standard Reference Material (SRM), supplied by National Bureau Standard (NBS), anthracene [CAS 120-12-7] (zone-refined, 99 + %), and naphthalene [CAS 91-20-3] (scintillation grade 99 + %), both supplied by Aldrich Chemical Co.

Rotating Bomb Calorimetry. The measurements of the energies of combustion of the two sulfur compounds were carried out in an isoperibol rotating-bomb calorimeter (formerly developed by Professor Stig Sunner at the University of Lund, Sweden, and installed in our department), with a platinum-lined bomb with an internal volume of 0.258 dm^3. The details of the apparatus have been described in the literature,[6] the reason why only some important remarks related with the experiments will be given here. The accurate numerical calculation of the corrected temperature rise in the isoperibol calorimetry was carried out by means of the Labtermo program.[7,8]

The energy equivalent of the calorimeter, ε(calor), was determined using benzoic acid NBS SRM 39j, having a massic energy of combustion, $\Delta_c u$, under standard bomb conditions of $-(26\,434 \pm 3)\ \text{J}\cdot\text{g}^{-1}$. Calibration experiments were carried out in oxygen at a pressure of 3.04 MPa (preliminary bomb flushing) with 1.00 cm^3 of deionized water added to the bomb, without rotation of the bomb. The value obtained for the energy equivalent, from six experiments, was $\varepsilon(\text{calor}) = (25\,157.4 \pm 1.1)\ \text{J}\cdot\text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean, for an average mass of water added to the calorimeter of 5217.0 g. There were no changes in the calorimetric system during the studies entailed for the two heterocycles, and therefore, it was not necessary to make a new calibration when going from the first to the second compound.

The general procedure followed for the combustion of the organosulfur compounds was that described by Waddington et al.[9] For the combustion experiments, the samples of the tetrahydrothio-γ-pyrone and thioxanthone were pressed into pellets. As the tetrahydrothio-γ-pyrone compound is volatile at room temperature, the samples were enclosed into polyester bags made from Melinex, using the technique described by Skinner and Snelson.[10] For each experiment, a volume of water was added to the bomb, and the bomb was charged to a pressure of 3.04 MPa with oxygen without flushing, ensuring sufficient amounts of nitrogen oxides to oxidize the sulfur quantitatively to sulfur trioxide. The energy of reaction was always referred to the final temperature of 298.15 K. Rotation of the bomb was started when the temperature rise in the main period reached about 63 % of its final value and continued until the end of the experiment, ensuring a homogeneous solution of H_2SO_4(aq) in the bomb at the conclusion of the measurements. After the calorimetric measurements, the combustion products were checked for unburned carbon and other products of incomplete combustion, and in all cases, none were detected. The nitric acid formed due to the presence of nitrogen residues in the oxygen, used in the fulfillment of the bomb, was determined by the Devarda alloy method.[11] The amount of sulfuric acid was obtained by difference. Due to the relatively large amount of water used to ensure homogeneous H_2SO_4(aq) in the combustion experiments, no carbon dioxide analyses were made.

Calvet Microcalorimetry. The standard ($p° = 0.1$ MPa) molar enthalpy of sublimation of the compounds was measured by the vacuum drop microcalorimetric technique described by Skinner et al. for the study of solids.[12]

The measurements were performed with a Calvet high-temperature microcalorimeter (Setaram HT1000) with the vacuum promoted by rotary and vapor diffusion pumps. The details of the apparatus and of the technique are in the literature.[13]

The temperature, T, of the hot reaction vessel of the calorimeter was predefined for the sublimation study of each compound. In the case of tetrahydrothio-γ-pyrone, the temperature was 324.46 K, while in the case of thioxanthone, it was 442.68 K.

In each of the sublimation experiments, two thin glass capillary tubes—the sample and the reference capillary tubes—were used. They were sealed at one end and dropped (from room temperature) into the hot reaction vessel in the calorimeter held at the predefined temperature, T, and then removed from the hot zone by vacuum. The amount of the samples ranged from (3 to 4) mg for tetrahydrothio-γ-pyrone and from (3 to 5) mg for thioxanthone. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized by dropping tubes of nearly equal mass, to within (1 ± 10^{-4}) g, into each of the twin calorimetric cells.

The microcalorimeter was calibrated in situ for the different temperatures by performing sublimation experiments with reference materials, following a procedure identical to that described above for the compounds. For the sublimation experiments of tetrahydrothio-γ-pyrone, the value of the calibration constant of the calorimeter was $k_{\text{cal}} = 1.0062 \pm 0.0045$, obtained as the average of six independent calibration experiments with naphthalene, using its reported standard ($p° = 0.1$ MPa) molar enthalpy of sublimation at $T = 298.15$ K, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}} = (72.51 \pm 0.12)\ \text{kJ}\cdot\text{mol}^{-1}$.[14] For the enthalpy sublimation measurements of thioxanthone at $T = 442.68$ K, the constant of the microcalorimeter, determined using anthracene, was $k_{\text{cal}} = 0.9936 \pm 0.0049$, obtained as the average of six independent calibration experiments using the reported standard ($p° = 0.1$ MPa) molar enthalpy of sublimation at $T = 298.15$ K, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}} = (100.4 \pm 0.4)\ \text{kJ}\cdot\text{mol}^{-1}$.[15]

X-ray Data Collection and Structure Refinement. Crystals of tetrahydrothio-γ-pyrone were obtained from sublimation. They were monoclinic, space group $P2_1/c$, cell volume $V = 562.49(13)\ \text{Å}^3$, $a = 6.9044(12)$ Å, $b = 5.3740(6)$ Å, $c = 15.1631(16)$ Å, and $\beta = 91.220(14)°$ (uncertainties in parentheses). There are four molecules per unit cell, with a calculated density of $1.324\ \text{g}\cdot\text{cm}^{-3}$. Diffraction data were collected at 293 K with a Gemini PX Ultra equipped with Cu Kα radiation ($\lambda = 1.54184$ Å). A total of 1925 independent reflections were measured, of which 1757 were observed ($I > 2\sigma(I)$). The structure was solved by direct methods using SHELXS-97[16] with atomic positions and displacement parameters refined with SHELXL-97.[17] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined freely with isotropic displacement parameters. The refinement converged to $R(\text{all data}) = 0.0633$ and $wR^2(\text{all data}) = 0.1388$.

Full details of the data collection and refinement and tables of atomic coordinates, bond lengths and angles, and torsion angles have been deposited with the Cambridge Crystallographic Data Centre (CCDC 773636).

Computational Section

The total energies of all compounds considered in this work were calculated using the G3(MP2)//B3LYP method,[18] a variation of Gaussian-3 (G3) theory.[19] In this composite technique, the total energy of a given molecular species is obtained by a sequence of well-defined molecular orbital calculations. The first step of this method consists of the optimization of the molecular geometry and calculation of the vibrational frequencies with the hybrid B3LYP method[20,21] with the 6-31G(d) basis set. Then, a series of single-point energy calculations are carried out at higher levels of theory that include only valence electrons in the treatment of electron correlation (frozen core). The first higher-level calculation is at the quadratic configuration interaction QCISD(T)[22] with the 6-31G(d) basis set, which is then followed by a second-order Møller−Plesset level (MP2),[23] frozen core (FC), single-point calculation with the GTMP2Large basis set. The G3(MP2)//B3LYP energy at $T = 0$ K considers the QCISD(T)/6-31G(d) energy which is corrected by the energetic difference on going from MP2(FULL)//6-31G(d) to MP2(FC)//GTMP2Large, with spin−orbit correction, ΔE(SO), that is included only for atomic species, higher level correction (HLC) for molecules, and also the zero point energy correction E(ZPE), obtained from scaled B3LYP/6-31G(d) frequencies (scale factor 0.9614[24]). The energy value of the total energy at $T = 0$ K is then corrected for $T = 298.15$ K by introducing the vibrational term computed also at the B3LYP/6-31G(d) and the translational, rotational, and pV terms. Finally, the harmonic vibrational frequencies, determined at the B3LYP/6-31G(d) level, are used to confirm that all of the structures considered correspond to real minima on the potential energy surface.

The enthalpies of formation in the gas phase for the titled compounds were estimated from the calculated enthalpies of several gas-phase working reactions using the experimental standard molar gas-phase enthalpies of formation of the atoms and molecules there included, chosen on the basis of experimental thermochemical data availability. It must be noticed that some of the reactions are not isodesmic and that some errors due to the consideration of different bonds in the reactants and in the products may not be compensated (cf. bonds between atoms are not considered in the products of the reactions described by eqs 7 and 10). Therefore, to reduce the extension of those errors, we used the empirical correction procedure developed by Anantharaman and Melius,[25] i.e., the bond additivity correction (BAC) scheme, where atomic, molecular, and bondwise corrections are subtracted from the calculated enthalpy of formation of the compound derived from its reaction of atomization.

All calculations were done with the Gaussian-03 computer program.[26]

Results and Discussion

Enthalpies of Formation in the Crystalline Phase. In the combustion experiments with the organosulfur compounds, the products of the combustion process consist of a gaseous phase and an aqueous mixture of sulfuric acid for which the thermodynamics properties are known. The combustion reactions for tetrahydrothio-γ-pyrone and for thioxanthone are presented by the following equations, respectively

$$\mathrm{C_5H_8OS(cr) + 8O_2(g) + 112H_2O(l) \rightarrow 5CO_2(g) + H_2SO_4\cdot 115H_2O(aq)} \quad (1)$$

$$\mathrm{C_{13}H_8OS(cr) + 16O_2(g) + 112H_2O(l) \rightarrow 13CO_2(g) + H_2SO_4\cdot 115H_2O(aq)} \quad (2)$$

The energy associated with the isothermal bomb process, ΔU(IBP), was calculated through

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(\mathrm{H_2O, l})\Delta m(\mathrm{H_2O})\}\Delta T_{\mathrm{ad}} + (T_{\mathrm{i}} - 298.15)\varepsilon_{\mathrm{i}} + (298.15 - T_{\mathrm{i}} - \Delta T_{\mathrm{ad}})\varepsilon_{\mathrm{f}} + \Delta U(\mathrm{ign}) \quad (3)$$

where ΔT_{ad} is the calorimeter temperature corrected for the heat exchange, work of stirring, and frictional work of bomb rotation; $\Delta m(\mathrm{H_2O})$ represents the deviation of the mass of water added to the calorimeter from 5217.0 g, the water assigned to ε(calor); T_{i} is the initial temperature rise; ε_{i} and ε_{f} are the energies equivalent of the contents in the initial and final states, respectively; ΔU(ign) is the electric energy for the ignition; and $c_p(\mathrm{H_2O, l})$ is the massic heat capacity at constant pressure for liquid water. Standard state corrections or Washburn corrections, ΔU_{Σ}, were calculated as recommended in the literature.[27,28] The corrections for nitric acid formation were based on the value $-59.7\ \mathrm{kJ\cdot mol^{-1}}$, which is the molar energy of formation of $0.1\ \mathrm{mol\cdot dm^{-3}}$ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2(g)}$, $\mathrm{O_2(g)}$, and $\mathrm{H_2O(l)}$.[29] For the cotton thread fuse of empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, $-\Delta_c u^o = 16240\ \mathrm{J\cdot g^{-1}}$,[30] a value that was previously confirmed in our laboratory. The value for the pressure coefficient of specific energy $(\partial u/\partial p)_T$ was assumed to be $-0.2\ \mathrm{J\cdot g^{-1}\cdot MPa^{-1}}$, at $T = 298.15$ K, a typical value for most organic compounds.[31] The weights of the compounds were reduced to the true mass in vacuum, using the following specific densities: $1.496\ \mathrm{g\cdot cm^{-3}}$ for thioxanthone[32] and $1.324\ \mathrm{g\cdot cm^{-3}}$ for tetrahydrothio-γ-pyrone, determined in this work.

From the individual values of the standard ($p° = 0.1$ MPa) massic energy of combustion, $\Delta_c u°$, for each experiment, the mean value and the corresponding standard deviation of the mean were calculated (the overall results for tetrahydrothio-γ-pyrone and thioxanthone are presented in Tables S1 and S2, respectively, of the Supporting Information). Table 1 lists the mean value of the standard ($p° = 0.1$ MPa) massic energy of combustion, $\langle\Delta_c u^o(\mathrm{cr})\rangle$, and the derived molar energy, $\Delta_c U^o_m(\mathrm{cr})$, and enthalpy, $\Delta_c H^o_m(\mathrm{cr})$, of combustion, as well as the standard ($p° = 0.1$ MPa) molar enthalpy of formation $\Delta_f H^o_m(\mathrm{cr})$, for crystalline compounds. In accordance with the normal thermochemical practice, the uncertainties assigned to the standard ($p° = 0.1$ MPa) molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainty of the calibration. To derive $\Delta_f H^o_m$ from $\Delta_c H^o_m$, the standard ($p° = 0.1$ MPa) molar enthalpies of formation of $\mathrm{H_2O(l)}$, $\mathrm{CO_2(g)}$, and $\mathrm{H_2SO_4}$ in 115 $\mathrm{H_2O(l)}$, at $T = 298.15$ K, respectively, $-(285.830 \pm 0.042)\ \mathrm{kJ\cdot mol^{-1}}$,[33] $-(393.51 \pm 0.13)\ \mathrm{kJ\cdot mol^{-1}}$,[33] and $-(887.81 \pm 0.01)\ \mathrm{kJ\cdot mol^{-1}}$,[29] were used.

Enthalpies of Sublimation. Results of Calvet microcalorimetry measurements of the enthalpy of sublimation of thioxanthone and tetrahydrothio-γ-pyrone are given in Table 2. The observed enthalpy of sublimation, at the experimental temperature T, $\Delta^{\mathrm{g},T}_{\mathrm{cr},298.15\mathrm{K}}H^o_m$, corresponds to the mean of seven experiments for tetrahydrothio-γ-pyrone and five experiments for thioxanthone, with uncertainties given by their standard deviations. This parameter was corrected to $T = 298.15$ K by

Table 1. Mean Standard ($p^\circ = 0.1$ MPa) Massic Energy of Combustion, $\langle\Delta_c u^o(\text{cr})\rangle$, and Derived Molar Energy of Combustion, $\Delta_c U^o_m(\text{cr})$, Molar Enthalpy of Combustion, $\Delta_c H^o_m(\text{cr})$, and Molar Enthalpy of Formation, $\Delta_f H^o_m(\text{cr})$, for Crystalline Tetrahydrothio-γ-pyrone and Thioxanthone, at $T = 298.15$ K

compound	$\langle\Delta_c u^o(\text{cr})\rangle$ $\text{J}\cdot\text{g}^{-1}$	$\Delta_c U^o_m(\text{cr})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_c H^o_m(\text{cr})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H^o_m(\text{cr})$ $\text{kJ}\cdot\text{mol}^{-1}$
tetrahydrothio-γ-pyrone	− 29844.9 ± 3.9	− 3467.4 ± 1.3	− 3474.9 ± 1.3	− 238.0 ± 1.4
thioxanthone	− 32218.5 ± 1.7	− 6838.9 ± 1.2	− 6846.4 ± 1.2	− 14.6 ± 2.1

Table 2. Standard ($p^\circ = 0.1$ MPa) Molar Enthalpy of Sublimation, $\Delta^g_{cr}H^o_m$, for Tetrahydrothio-γ-pyrone and for Thioxanthone, at $T = 298.15$ K, Determined by Calvet Microcalorimetry

compound	number of experiments	T/K	$\Delta^{g,T}_{cr,298.15\text{K}}H^o_m$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta^{T}_{298.15\text{K}}H^o_m(\text{g})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta^g_{cr}H^o_m(298.15\text{ K})$ $\text{kJ}\cdot\text{mol}^{-1}$
tetrahydrothio-γ-pyrone	7	324.46	76.6 ± 0.6	3.2237 ± 0.0003[a]	73.4 ± 1.4
thioxanthone	5	442.68	141.9 ± 0.4	35.4090 ± 0.0004[a]	106.5 ± 1.2

[a] Uncertainties of the computational method and scaling factor are not included (see text).

eq 4 using the molar heat capacity in the gaseous phase for tetrahydrothio-γ-pyrone and thioxanthone given by eqs 5 and 6, respectively, which were derived from statistical thermodynamics using the vibrational frequencies calculated at the B3LYP/6-31G(d) level.[34] The correlation coefficients (R^2) of both equations are equal to 0.9999. The calculated molar heat capacities in the gaseous phase for tetrahydrothio-γ-pyrone (between (150 and 550) K) and for thioxanthone (between (250 and 650) K) are given in Table S3 of the Supporting Information.

$$\Delta^{T}_{298.15\text{K}}H^o_m(\text{g}) = \int^{T}_{298.15\text{K}} C^o_{p,m}(\text{g})\text{d}T \tag{4}$$

$$C^o_{p,m}(\text{g})/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = -6.44446\cdot10^{-7}(T/\text{K})^3 + 5.59288\cdot10^{-4}(T/\text{K})^2 + 1.89177\cdot10^{-1}(T/\text{K}) + 28.8121 \tag{5}$$

$$C^o_{p,m}(\text{g})/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = -4.62210\cdot10^{-9}(T/\text{K})^3 - 5.08996\cdot10^{-4}(T/\text{K})^2 + 9.54757\cdot10^{-1}(T/\text{K}) - 37.6996 \tag{6}$$

The uncertainties associated with the standard ($p^\circ = 0.1$ MPa) molar enthalpies of sublimation, at $T = 298.15$ K, $\Delta^g_{cr}H^o_m(298.15\text{ K})$, are twice the standard deviations of the mean and include the estimated uncertainties associated with the calibration procedures and the molar heat capacities of the compounds in the gaseous state.

Enthalpies of Formation in the Gaseous Phase. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, of the studied compounds were derived from the experimental values of the enthalpies of sublimation and formation in the crystalline phase, at the same temperature. So, for tetrahydrothio-γ-pyrone the result $\Delta_f H^o_m(\text{g}) = (-164.6 \pm 2.0)\ \text{kJ}\cdot\text{mol}^{-1}$ is obtained from the experimental $\Delta_f H^o_m(\text{cr}) = (-238.0 \pm 1.4)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta^g_{cr}H^o_m = (73.4 \pm 1.4)\ \text{kJ}\cdot\text{mol}^{-1}$, while for thioxanthone, the experimental $\Delta_f H^o_m(\text{cr}) = (-14.6 \pm 2.1)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta^g_{cr}H^o_m = (106.5 \pm 1.2)\ \text{kJ}\cdot\text{mol}^{-1}$ yield the result $\Delta_f H^o_m(\text{g}) = (91.9 \pm 2.4)\ \text{kJ}\cdot\text{mol}^{-1}$.

As it was said above, some experimental studies have been carried out in the past for some sulfur heterocycles. In the case of thioxanthone, Sabbah et al.[35] performed a detailed thermodynamic study employing combustion calorimetry, sublimation calorimetry, differential thermal analysis, and heat capacity measurements. They reported an experimental value of the standard molar enthalpy of formation in the gas phase, $\Delta_f H^o_m(\text{g}) = (94.3 \pm 3.6)\ \text{kJ}\cdot\text{mol}^{-1}$, which is in agreement with our experimental value, considering the uncertainty associated. However, analyzing in more detail their standard molar enthalpies of formation in the crystalline state, $\Delta_f H^o_m(\text{cr}) = (-20.5 \pm 3.6)\ \text{kJ}\cdot\text{mol}^{-1}$, and of sublimation, $\Delta^g_{cr}H^o_m = (114.81 \pm 0.41)\ \text{kJ}\cdot\text{mol}^{-1}$, and comparing them with the values determined in this work, it is possible to notice important differences, $\Delta = -5.9\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta = 8.3\ \text{kJ}\cdot\text{mol}^{-1}$, for the enthalpies of formation in the crystalline state and of sublimation, respectively. For tetrahydrothio-γ-pyrone, Geiseler et al.[36] presented the following values, $\Delta_c H^o_m(\text{cr}) = (-3485.3 \pm 2.1)\ \text{kJ}\cdot\text{mol}^{-1}$, which according to our calculations will yield $\Delta_f H^o_m(\text{cr}) \approx -227.6\ \text{kJ}\cdot\text{mol}^{-1}$ (it was not possible to calculate the uncertainty associated), $\Delta^g_{cr}H^o_m = (72.6 \pm 1.7)\ \text{kJ}\cdot\text{mol}^{-1}$, and $\Delta_f H^o_m(\text{g}) = -155.0\ \text{kJ}\cdot\text{mol}^{-1}$. Comparing the results from the present work with those from the Geiseler's study, an excellent agreement is found between the enthalpies of sublimation with a difference, Δ, of $-0.8\ \text{kJ}\cdot\text{mol}^{-1}$, while a considerable difference is found between the enthalpies of formation in the crystalline phase ($\Delta = +10.4\ \text{kJ}\cdot\text{mol}^{-1}$), leading to distinct values for the standard molar enthalpy of formation in the gas phase ($\Delta = +9.6\ \text{kJ}\cdot\text{mol}^{-1}$).

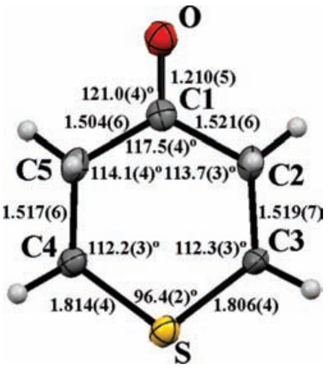


Figure 1. Geometry of the tetrahydrothio-γ-pyrone molecule in the crystalline phase, showing the atom-labeling scheme (displacement ellipsoids are drawn at the 50 % probability level; hydrogen atoms are represented by circles of arbitrary size). Selected bonds are given in Å.

In a subsection below, the present gaseous enthalpic values for tetrahydrothio-γ-pyrone and thioxanthone will be compared with standard molar enthalpies of formation in the gas phase calculated with state-of-the-art computational thermochemistry approaches.

Crystallographic Data. The geometry of the tetrahydrothio-γ-pyrone molecule and the correspondent bond lengths and angles are presented in Figure 1. This molecule presents C_1 symmetry. The thiopyran ring assumes a chair conformation; dihedral angles: $a-b-c-d$, -132.4° and $b-c-d-e$, -58.5°

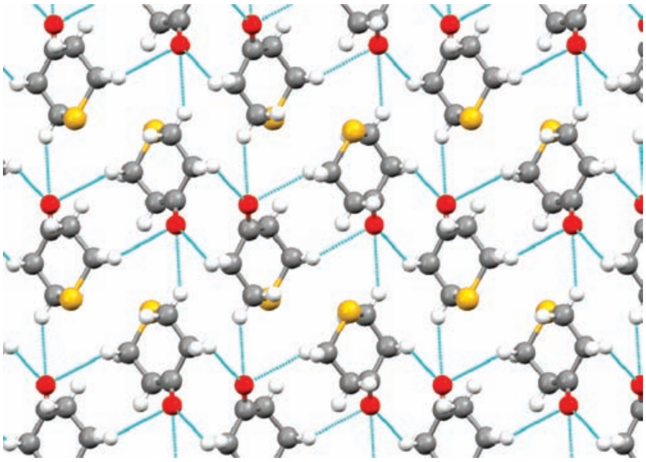


Figure 2. Crystal packing of tetrahydrothio-γ-pyrone, viewed along the *b*-axis, showing the short contacts of the oxygen atom.

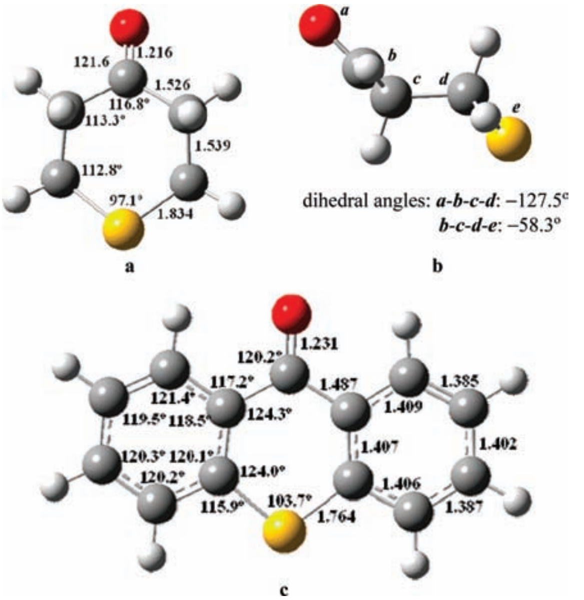


Figure 3. Front (a) and side (b) views of the geometry of the gaseous tetrahydrothio-γ-pyrone molecule and front view of the geometry of the gaseous thioxanthone molecule (c) optimized at the B3LYP/6-31G(d) level of theory. Selected bonds are given in Å and angles in degrees.

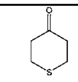
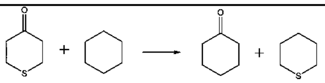
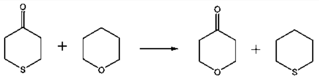
(for labeling see Figure 3b). The C−S bond lengths of (1.806(4) and 1.814(4)) Å are in agreement with the expected value of 1.81 Å.[37] The C−S−C angle of 96.4° is slightly shorter than the values 97.5° and 98.7° observed in the crystal structures of other thiopyran derivatives.[37] Moreover, the oxygen atom establishes short contacts with hydrogen atoms of three distinct neighboring molecules [C−H···O distances of (2.61, 2.67, and 2.67) Å] (Figure 2). On the contrary to the chair conformation of tetrahydrothio-γ-pyrone, the three-ring system of thioxanthone derivatives is essentially planar. Figure S1, given in Supporting Information, shows a view of 3-methyl-9-oxothioxanthene, as determined by X-ray crystallography,[38] where selected bond lengths and angles are indicated. The central pyranoid ring has a partial aromatic character with the bond lengths shorter than the corresponding bonds in the tetrahydrothio-γ-pyrone. Figures 1 and 2 were prepared using mercury.[39]

Computational Results. Selected geometrical parameters of the structures of the isolated tetrahydrothio-γ-pyrone and thioxanthone molecules optimized at the B3LYP/6-31G(d) level of theory are given in Figure 3 (full geometry details are given in Tables S4 and S5 of the Supporting Information, respectively). The most stable structure optimized for tetrahydrothio-γ-pyrone is a chair conformation, with a C_1 symmetry (cf., Figures 3a and 3b). Comparing the gaseous optimized geometry and the crystal structure obtained for tetrahydrothio-γ-pyrone, there are some differences, but not significant, between the bond angles and the bond distances. In general the bond distances are higher in the gaseous structure; to note, the C−S−C angle in the crystal structure is smaller, and the opposite C−C−C angle is slightly higher. The similarities between the structures of tetrahydrothio-γ-pyrone in gaseous and crystalline phases, i.e., molecular shape, symmetry, and conformation, indicate no appreciable crystal field effects.[40]

The isolated thioxanthone molecule obtained by B3LYP/6-31G(d) (cf. Figure 3c) is totally planar and has a C_s symmetry. This structure compares satisfactorily with the experimental one obtained by gas-phase electron diffraction.[41] Comparing the crystal[32] and gaseous (this work) structures determined for thioxanthone, there are not any important structural differences suggesting the absence of crystal field effects. Comparison of the gaseous structures of thioxanthone, thioxanthene,[2] xanthone,[1] and xanthene,[3] it is concluded that the dihedral angles between the two benzene rings in thioxanthone and xanthone are notably larger than those found in the other two molecules. The flatness of the molecular planes of xanthone and thioxanthone is most probably due to the sp^2 hybridization of the carbonyl group.[41]

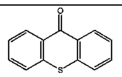
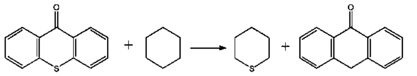
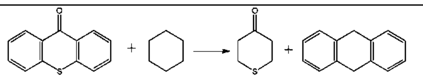
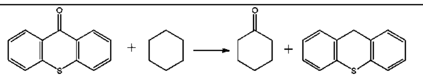
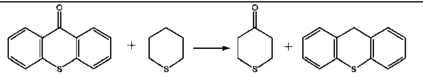
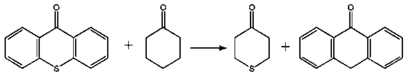
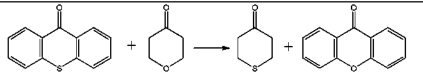
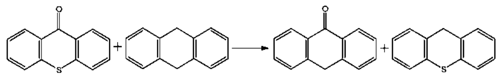
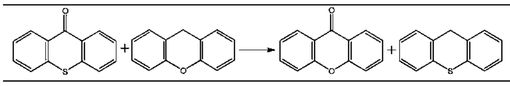
The numerical values calculated for the enthalpies of reaction and of formation, at T = 298.15 K, of the compounds tetrahydrothio-γ-pyrone and thioxanthone, considering different gas-phase working reactions, appear in Tables 3 and 4, respectively, together with deviations from the calculated and experimental $\Delta_f H_m^\circ(g)$. The G3(MP2)//B3LYP absolute enthalpies and the experimental gas-phase enthalpies of formation, at the T = 298.15 K, for all the species considered in this work (title compounds and auxiliary species appearing in the equations in Tables 3 and 4) are given as Supporting Information (Table S6). In the calculation of the enthalpy of formation of the tetrahydrothio-γ-pyrone species, three working reactions were considered, yielding values ranging from (−162.0 to −167.8) kJ·mol^{-1}, leading to a mean value of −164.1 kJ·mol^{-1}, which is in excellent agreement with the experimental result, $\Delta_f H_m^\circ(g) = -(164.6 \pm 2.0)$ kJ·mol^{-1}. Nine working reactions were considered for the calculation of the standard molar enthalpy of formation of thioxanthone in the gas phase (cf. Table 4). The uncorrected value obtained with the atomization reaction described by eq 10 is 75.7 kJ·mol^{-1}, which is far from the experimental result ($\Delta_f H_m^\circ(g) = (91.9 \pm 2.4)$ kJ·mol^{-1}). Upon the introduction of BAC corrections, the calculated enthalpy of formation of thioxanthone becomes 80.9 kJ·mol^{-1}, which is still far from the experimental result ($\Delta = 11.0$ kJ·mol^{-1}). Thus, at this point, one may conclude that the computational approach is not adequate to deal with these kinds of compounds or that the use of the BAC scheme, for compensation of different bonds between reactants and products of reaction, is insufficient in this case. As it will be shown below, it seems that the first of these two hypotheses is definitely wrong and that the G3(MP2)//B3LYP approach together with homodesmotic reactions and good values for the experimental enthalpies of formation of the auxiliary compounds is entirely acceptable for dealing with these sulfur-containing heterocycles. An inspection of the other calculated values in Table 4 shows that using the working reactions described by eqs 12 to 14, 16, and 18 the calculated enthalpies of formation—values between (88.9 to 96.4)

Table 3. Working Reactions for Tetrahydrothio-γ-pyrone and Correspondent Values for the Enthalpies of Reaction and Formation in the Gaseous Phase, at $T = 298.15$ K

Working reactions		ΔH_R(g) / kJ.mol^{-1}	$\Delta_f H_m^o$(g) / kJ.mol^{-1}	Δ[a] / kJ.mol^{-1}
 → 5 C + 8 H + S + O	(7)	6020.22	− 166.7[b] − 162.6[c]	2.1 2.0
	(8)	− 4.30	− 162.0	2.6
	(9)	− 0.95	− 167.8	3.2
			<− 164.1[d]>	0.5

[a] Δ corresponds to $|\Delta_f H_m^o(\text{exp,g}) - \Delta_f H_m^o(\text{calc,g})|$. [b] Calculated uncorrected gas-phase enthalpy of formation. [c] Calculated BAC-corrected gas-phase enthalpy of formation. [d] Mean value calculated from the values of the enthalpies from eqs 7 (corrected value), 8, and 9.

Table 4. Working Reactions for Thioxanthone and Correspondent Values for the Enthalpies of Reaction and Formation in the Gaseous Phase, at $T = 298.15$ K

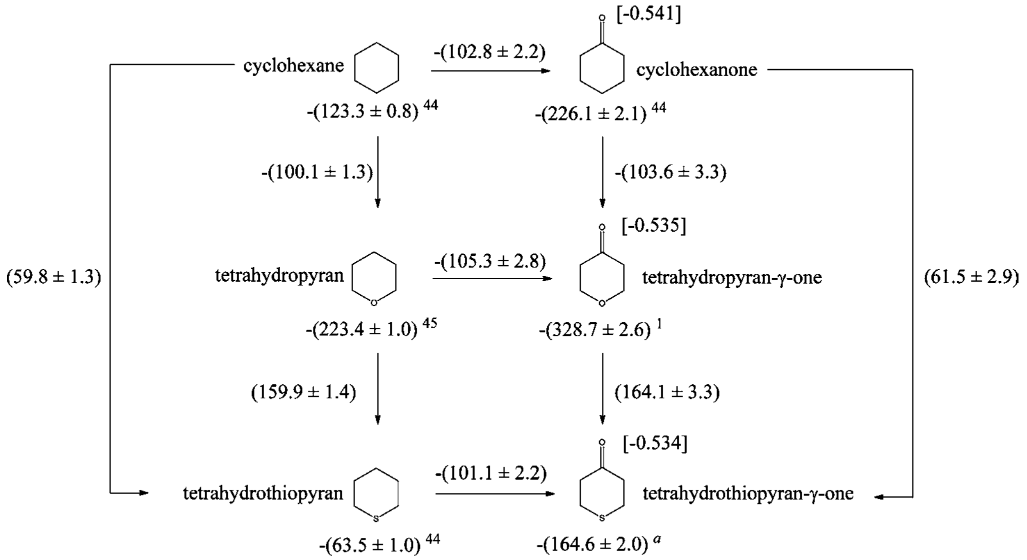
Working reactions		ΔH_R(g) / kJ.mol^{-1}	$\Delta_f H_m^o$(g) / kJ.mol^{-1}	Δ[a] / kJ.mol^{-1}
 → 13 C + 8 H + S + O	(10)	11511.15	75.7[b] 80.9[c]	16.2 11.0
	(11)	6.29	84.9[d] (76.9[e]) (74.6[f])	7.0 15.0 17.3
	(12)	27.42	91.0	0.9
	(13)	24.42	91.5	0.4
	(14)	28.73	88.9	3.0
	(15)	10.59	82.3[d] (74.3[e]) (72.0[f])	9.6 17.6 19.9
	(16)	− 26.28	96.4	4.5
	(17)	7.59	82.8[d] (74.8[e]) (72.5[f])	9.1 17.1 19.4
	(18)	− 10.55	93.5	1.6
			<92.3[g]>	0.4

[a] Δ corresponds to $|\Delta_f H_m^o(\text{exp,g}) - \Delta_f H_m^o(\text{calc,g})|$. [b] Calculated uncorrected gas-phase enthalpy of formation. [c] Calculated BAC-corrected gas-phase enthalpy of formation. [d] Value estimated using $\Delta_f H_m^o$(g) for anthrone from ref 3. [e] Value estimated using $\Delta_f H_m^o$(g) for anthrone from ref 42. [f] Value estimated using $\Delta_f H_m^o$(g) for anthrone from ref 43. [g] Mean value does not consider the enthalpies from eqs 10, 11, 15, and 17.

kJ·mol^{-1}—are in a very good agreement with the experimental $\Delta_f H_m^o$(g). However, when reactions described by eqs 11, 15, and 17 are considered, i.e., those anchored on the enthalpy of formation of anthrone, it is possible to verify very large differences between the experimental and the calculated values for thioxanthone. In fact, using any of the experimental results available in the literature for anthrone, i.e., those from Watik and Sabbah,[42] $\Delta_f H_m^o$(g) = (23.4 ± 2.2) kJ·mol^{-1}, or from Verevkin,[43] $\Delta_f H_m^o$(g) = (21.1 ± 1.5) kJ·mol^{-1}, the difference between the experimental and the calculated values for thioxanthone is very large [(15.0 to 19.9) kJ·mol^{-1}, respectively]. Furthermore, using our own experimental result, $\Delta_f H_m^o$(g) = (31.4 ± 3.2) kJ·mol^{-1},[3] the difference between the experimental and calculated values becomes smaller but noticeable (7.0 kJ·mol^{-1}), suggesting a deficient compensation for different bonds between reactants and products in working reactions involving anthrone.

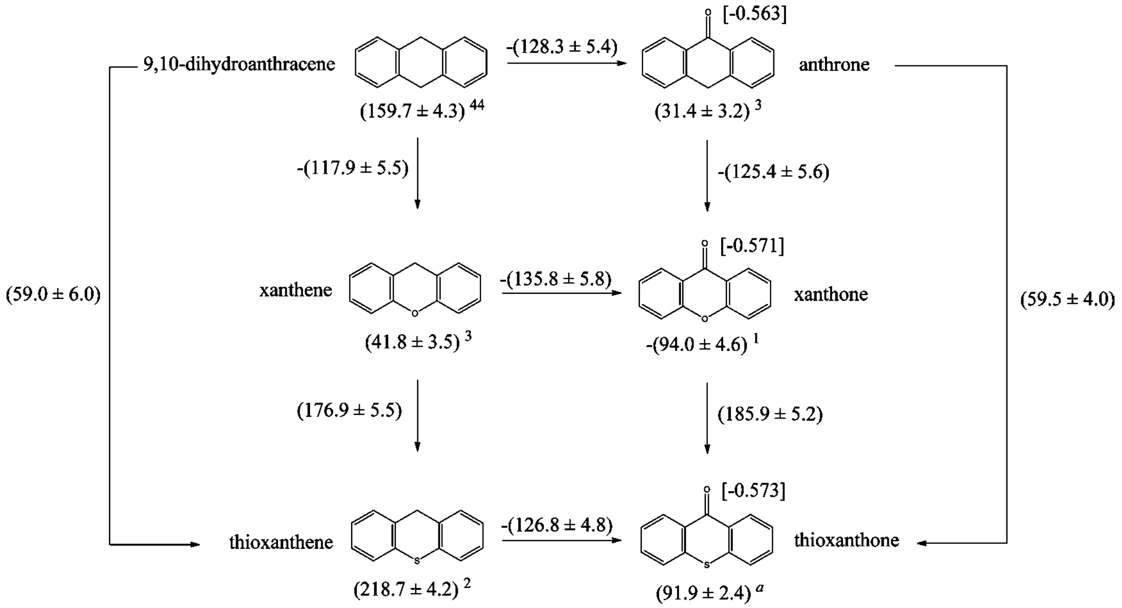
Final Remarks. In Schemes 2 to 5 are presented the standard molar enthalpies of formation in the gaseous phase and the calculated values of the enthalpic increments associated with the process of replacing a $-CH_2-$ group by a $-C(=O)-$, together with the natural population charge of the oxygen's carbonyl group, determined by computational studies using the natural population analysis (NPA) of Natural Bond Orbital (NBO) theory. Additionally, in Schemes 2 and 3 are reported the enthalpic increments associated to the substitution of a

Scheme 2. Enthalpic Increments (Values in kJ·mol^{-1}) for the Following Group Substitutions in Monocyclic Compounds[b]



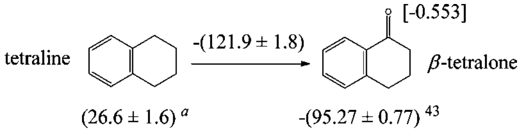
[a] This work. [b] $-CH_2-$ by $-C(=O)-$ (horizontal arrows); $-CH_2-$ by $-O-$ (inner top vertical arrows); $-O-$ by $-S-$ (inner bottom vertical arrows); $-CH_2-$ by $-S-$ (left side and right side arrows). Oxygen natural population charge appears inside square brackets.

Scheme 3. Enthalpic Increments (Values in kJ·mol^{-1}) for the Following Group Substitutions in Tricyclic Compounds[b]



[a] This work. [b] $-CH_2-$ by $-C(=O)-$ (horizontal arrows); $-CH_2-$ by $-O-$ (inner top vertical arrows); $-O-$ by $-S-$ (inner bottom vertical arrows); $-CH_2-$ by $-S-$ (left side and right side arrows). Oxygen natural population charge appears inside square brackets.

Scheme 4. Enthalpic Increments (Values in kJ·mol^{-1}) for the Substitution of a $-CH_2-$ Group by a $-C(=O)-$ Group in Bicyclic Compounds and Oxygen Natural Population Charge (Square Brackets)[a]

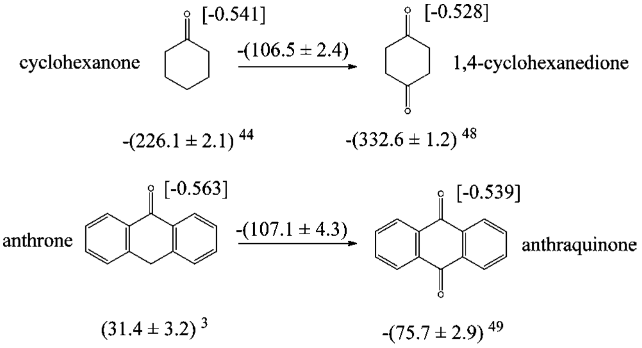


[a] Derived from $\Delta_f H_m^o(l) = -(28.6 \pm 1.0)$ kJ·mol^{-1},[46] and $\Delta_l^g H_m^o = (55.2 \pm 1.3)$ kJ·mol^{-1}.[47]

$-CH_2-$ group by $-O-$ or $-S-$ groups and also for the substitution of an $-O-$ group by an $-S-$ group in mono- and tricyclic compounds.

The substitution of the $-CH_2-$ group by a $-C(=O)-$ group, on saturated monocyclic compounds, Scheme 2, presents

Scheme 5. Enthalpic Increments (Values in kJ·mol^{-1}) for the Substitution of a $-CH_2-$ Group by a $-C(=O)-$ Group in Ketone Derivatives and Oxygen Natural Population Charge (Square Brackets)



identical increments in the order of (−101.1 to −105.3) kJ·mol^{-1}. In Scheme 3, dealing with tricyclic compounds, the same substitution yields enthalpic increments in the order of (−126.8 to −135.8) kJ·mol^{-1}, all higher than those for the monocyclic compounds, suggesting that the substitution is more favorable in tricyclic compounds. In the case of bicyclic compounds, Scheme 4, an intermediate situation relative to the two earlier schemes is found; i.e., the $-CH_2-$ by $-C(=O)-$ replacement has an enthalpic increment of −121.9 kJ·mol^{-1}. The enthalpic differences described can be understood if we consider the following: (i) the carbon atom in the methylene group is sp^3 hybridized with a tetrahedral shape, while in the carbonyl group it is sp^2 hybridized and in the same plane defined by the oxygen atom and the two neighboring carbons of the cycle; (ii) the oxygen atom is more electronegative than the carbon atom of the carbonyl group, causing an appreciable polarization of the carbon−oxygen double bond, with a partial positive charge on carbon and an equal amount of negative charge on oxygen; the compounds with larger polarization effects (charges of about (−0.56 to −0.57) *e*), according to natural population charges in the oxygen atom, have larger enthalpic increments (Scheme 3), while those with smaller polarization (charges of about (−0.53 to −0.54) *e*) have smaller enthalpic increments (Schemes 2 and 5); (iii) in the ketone polycyclic derivatives, electronic charge delocalization involving the π system(s) of the adjacent ring(s) is possible.

Interestingly, the second substitution of a $-CH_2-$ group by a $-C(=O)-$ group in cyclohexanone and anthrone, yielding 1,4-cyclohexanedione and anthraquinone, respectively (Scheme 5), has enthalpic increments of −106.5 kJ·mol^{-1} and −107.1 kJ·mol^{-1}, respectively, that are close to those found for the monocyclic compounds. The value of the last increment suggested that in anthraquinone there is a loss of importance of mesomeric effects and that only the inductive effects prevail, as suggested by comparison of the natural population charges (charges of about (−0.53 to −0.54) *e*) of the oxygen atoms in anthraquinone and in the monocyclic compounds.[44−49] Analyzing the enthalpic increments presented in Schemes 2 and 3 associated to the substitutions of a $-CH_2-$ unit by $-O-$ or $-S-$ groups or of an $-O-$ group by an $-S-$ group in mono- and polycyclic compounds, it is possible to extract the following conclusions: (i) the replacement of the $-CH_2-$ unit by an $-O-$ group presents the lowest enthalpic increments, while the higher increments are found for the replacement of an $-O-$ group by an $-S-$ group; (ii) the values of the enthalpic increments between mono- and polycyclic compounds differ slightly, except in the case of the replacement of a $-CH_2-$ unit by an $-S-$ group. Finally, the enthalpically less favorable substitutions of $-CH_2-$ or $-O-$ groups by $-S-$ are probably due to the much larger volume occupied by the sulfur atom when compared with those for the methylene group or the oxygen atom, which introduces destabilizing steric effects with the chemical vicinity.

Supporting Information Available:

Figure S1: Crystallographic structure of 3-methyl-9-oxothioxanthene. Table S1: Typical combustion results, at T = 298.15 K ($p°$ = 0.1 MPa), for tetrahydrothio-γ-pyrone. Table S2: Typical combustion results, at T = 298.15 K ($p°$ = 0.1 MPa), for tioxanthone. Table S3: Standard ($p°$ = 0.1 MPa) molar heat capacities in the gaseous phase for tetrahydrothio-γ-pyrone and thioxanthone. Table S4: Calculated bond distances (Å) and angles (°), by B3LYP/6-31G(d) level of theory, for tetrahydrothio-γ-pyrone in gaseous phase. Table S5: Calculated bond distances (Å) and angles (°), by the B3LYP/6-31G(d) level of theory, for thioxanthone in gaseous phase. Table S6: G3(MP2)//B3LYP enthalpies for tetrahydrothio-γ-pyrone, thioxanthone, and for the auxiliary species and the experimental gas-phase enthalpy of formation at T = 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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