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Energetic effects of ether and ketone functional groups in 9,10-dihydroanthracene compound

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ABSTRACT

The energetic effects caused by replacing one of the methylene groups in the 9,10-dihydroanthracene by ether or ketone functional groups yielding xanthene and anthrone species, respectively, were determined from direct comparison of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, of these compounds. The experimental static-bomb combustion calorimetry and Calvet microcalorimetry and the computational G3(MP2)//B3LYP method were used to get the standard molar gas-phase enthalpies of formation of xanthene, $(41.8 \pm 3.5)\ \mathrm{kJ \cdot mol^{-1}}$, and anthrone, $(31.4 \pm 3.2)\ \mathrm{kJ \cdot mol^{-1}}$. The enthalpic increments for the substitution of methylene by ether and ketone in the parent polycyclic compound (9,10-dihydroanthracene) are $-(117.9 \pm 5.5)\ \mathrm{kJ \cdot mol^{-1}}$ and $-(128.3 \pm 5.4)\ \mathrm{kJ \cdot mol^{-1}}$, respectively.

1. Introduction

Studies on the structural and energetic parameters of aromatic and non-aromatic heteropolycyclic compounds, both in the condensed and gaseous phases, are rather scarce when compared with the corresponding polycyclic hydrocarbons. Recently, some thermochemical data in particular for heteropolycyclic compounds containing oxygen and sulfur have been published [1–5]. Herewith, there is presented an experimental and computational thermochemical study of two tricyclic compounds, namely, anthrone ((10*H*)-9-anthracenone) and xanthene ((10*H*)-9-oxaanthracene), whose basic structure is the 9,10-dihydroanthracene moiety. As can be seen in figure 1, anthrone presents a ketone functional group in position 9, while xanthene possesses an oxygen atom inserted into the ring at the same position.

The literature has already some energetic data for the title compounds, which appear in table 1. The first experimental thermodynamic study for anthrone was carried out by Sabbah *et al.* [6,7], which was followed by another due to Verevkin [8] devoted to aromatic ketones. Despite noticeable differences in the standard molar enthalpies of formation in the crystalline phase and in the enthalpies of sublimation determined by these two groups, the enthalpies of formation in the gaseous phase are the same within the uncertainties associated with the results. Monte *et al.* [9] performed very recently a vapour pressure study of anthrone, using the Knudsen effusion technique, obtaining for the standard ($p^\circ = 0.1$ MPa) molar enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^\circ = (107.6 \pm 0.8\ \mathrm{kJ \cdot mol^{-1}})$, which is in perfect agreement with the value of Verevkin [8].

Based on computational studies, Notario *et al.* [10] reported two calculated results for the $\Delta_{\mathrm{f}} H_{\mathrm{m}}^\circ(\mathrm{g})$ for anthrone – the enthalpy of the reaction diphenylmethane + benzophenone → anthrone + 2 benzene was calculated using two different experimental values of the enthalpy of formation of diphenylmethane, in the liquid state, yielding the two different values for the enthalpy of formation of gaseous anthrone – both significantly different from the experimental values of Sabbah *et al.* [7] and Verevkin [8].

Previously, we have also detected some inconsistencies between the computational and experimental gas-phase standard molar enthalpies of formation of anthrone [4] when considering their published experimental values [6–8] on the calculation of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^\circ(\mathrm{g})$ of other compounds. For that reason, we decided to perform new experimental studies for this compound since its ther-

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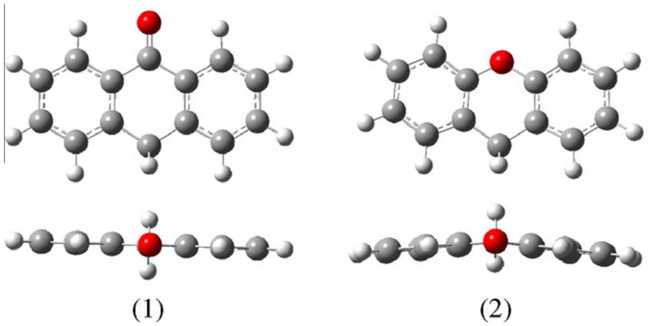


FIGURE 1. Views of the molecular structures of anthrone (1) and xanthene (2) optimized at the B3LYP/6-31G(*d*).

mochemical parameters are crucial for the calibration of computational approaches used for the estimation of thermodynamic properties of compounds derived from anthrone.

Xanthene is structurally similar to other compounds that we have been studying such as xanthone and thioxanthene [4,5]. Structural and thermochemical data are almost non-existent for xanthene derivatives and, to our best knowledge, there is only the work developed by Monte *et al.* [11] where is reported the $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\circ}$, for xanthene (9*H*-dibenzo[a,e]pyran) determined after vapour pressure measurements with the Knudsen effusion technique and the static apparatus. In the literature, there are also some data for an isomer of xanthene, dibenzopyran (6*H*-dibenzo[b,d]pyran), which differs by the way in which the central ring is fused to the other two rings (table 1). In the case of dibenzopyran (6*H*-dibenzo[b,d]pyran), the literature has values for its standard molar enthalpies of formation (condensed and gaseous phases) and of phase transition [12–15]. Some authors, erroneously reported the parameters outlined above as data for xanthene (9*H*-dibenzo[a,e]-pyran) [16].

In this work, we report the standard ($p^{\circ} = 0.1$ MPa) molar enthalpy of formation in the crystalline phase, $\Delta_{\rm f}H_{\rm m}^{\circ}({\rm cr})$, and the standard molar enthalpy of sublimation, $\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\circ}$, at $T = 298.15$ K, for anthrone and xanthene, determined by static-bomb combustion calorimetry and Calvet microcalorimetry techniques, respectively. From these two thermochemical parameters the $\Delta_{\rm f}H_{\rm m}^{\circ}({\rm g})$ was derived at the reference temperature. The composite G3(MP2)//B3LYP computational approach was used to optimize the structures of these two compounds and to calculate their $\Delta_{\rm f}H_{\rm m}^{\circ}({\rm g})$ values.

2. Experimental details

2.1. Materials

Anthrone (CAS Registry No. 90-44-8) and xanthene (CAS Registry No. 92-83-1) were obtained commercially from Aldrich Chemical Co., with mass fraction purities of 0.970 and 0.998, respectively.

The compounds used in the calibrations of the calorimetric systems were: benzoic acid [CAS Registry No. 65-85-0] supplied by National Bureau Standard (NBS), Standard Reference Material (SRM) 39j, anthracene [CAS Registry No. 120-12-7] (zone-refined, 0.99+) and naphthalene [CAS Registry No. 91-20-3] (scintillation grade 0.99+), both supplied by Aldrich Chemical Co.

2.2. Purification of the compounds

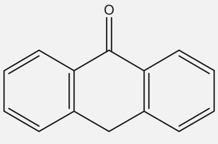
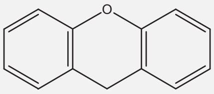
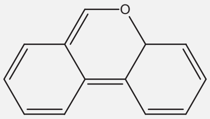
Before the calorimetric experiments, anthrone and xanthene were purified by repeated sublimations under reduced pressure. The purity of the samples was controlled by gas chromatography, using an Agilent 4890 apparatus equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m long, 0.530 mm i.d., 1.5 μm film thickness), and also by the ratio of carbon dioxide recovered in the combustion experiments.

2.3. Static bomb calorimetry

The energies of combustion of anthrone and xanthene were determined using an isoperibol calorimeter equipped with a twin valve static bomb (with an internal volume of 0.290 dm^3). The apparatus and the detailed procedure have been described previously [17–19].

The calorimetric system was calibrated using benzoic acid, NBS SRM 39j, having a massic energy of combustion, under bomb conditions, of $-(26434 \pm 3)$ J · g^{-1}. Calibration experiments were carried out in oxygen at a pressure of 3.04 MPa, with 1.00 cm^3 of deionised water added to the bomb. The calibration results were corrected to give the energy equivalent ε(calor) corresponding to an average mass of water added to the calorimeter of 2900.0 g. The calorimetric system has been calibrated before the study of each compound, since it has been necessary to do some repairs in the equipment between the two sets of experiments. The equivalent energies of the calorimeter during the study of anthrone and xanthene were $\varepsilon({\rm calor}) = 15551.7 \pm 1.2$ J · K^{-1} (from six experiments) and $\varepsilon({\rm calor}) = 15546.3 \pm 1.3$ J · K^{-1} (from eight experi-

TABLE 1
Thermochemical results available in the literature for anthrone, xanthene and dibenzopyran, at $T = 298.15$ K. Columns 3, 4, 5, respectively, are headed by the standard molar enthalpy of formation in the crystalline phase, standard molar enthalpy of sublimation, and the standard molar enthalpy of formation in the gas phase, all referred to $T = 298.15$ K.

Name and CAS Registry No.	Molecular structure	$\Delta_{\rm f}H_{\rm m}^{\circ}({\rm cr})/({\rm kJ \cdot mol^{-1}})$	$\Delta_{\rm cr}^{\rm g}H_{\rm m}^{\circ}/({\rm kJ \cdot mol^{-1}})$	$\Delta_{\rm f}H_{\rm m}^{\circ}({\rm g})/({\rm kJ \cdot mol^{-1}})$	References
Anthrone (90-44-8)		−79.9 ± 2.1	103.32 ± 0.63	23.4 ± 2.2	[6,7]
		−85.0 ± 1.2	106.10 ± 0.81	21.1 ± 1.5	[8]
			107.6 ± 0.8		[9]
				42.8 ± 3.5; 34.6[a]	[10]
Xanthene (9*H*-dibenzo[a,e]pyran) (92-83-1)			92.6 ± 0.1		[11]
Dibenzopyran (6*H*-dibenzo[b,d]pyran) (229-95-8)		−63.6 ± 4.0	112.1 ± 2.1	48.5 ± 5.0	[12–15]

[a] Calculated values.