Thermodynamic Study on the Sublimation of Anthracene-Like Compounds

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A Knudsen mass-loss effusion technique was used for measuring the vapor pressures at different temperatures of the following crystalline compounds: anthraquinone (CAS No. 84-65-1), between (377.06 and 395.03) K; anthrone (CAS No. 90-44-8), between (346.15 and 365.14) K; thianthrene (CAS No. 92-85-3), between (344.27 and 264.06) K; thioxanthone (CAS No. 492-22-8), between (369.12 and 387.20) K; and xanthone (CAS No. 90-47-1), between (342.22 and 362.22) K. From the temperature dependence of the vapor pressure of each crystalline compound, the standard ($p^o = 10^5$ Pa) molar enthalpies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived. The measured thermodynamic properties are compared with literature results for similar compounds, and correlations for estimation of the vapor pressures and enthalpy of sublimation for anthracene-like compounds are presented.

Introduction

In previous works our research group presented sublimation studies from vapor-pressure measurements for phenoxatiin,[1] xanthene,[1] and thioxanthene.[2] These compounds may be considered to be derived from anthracene after substituting the meso CH groups for others represented by X and Y in Figure 1, being X = O and Y = S for phenoxatiin, X = O and Y = CH_2 for xanthene, and X = S and Y = CH_2 for thioxanthene. Trying to develop a scheme for predicting the vapor pressures and enthalpies of sublimation of compounds with different combinations of CH_2, CO, S, and O in the positions X and Y, we collected literature values presented in Tables 5 and 6. After examining the existent literature values, we considered that the published results (both for enthalpy of sublimation and vapor pressures) for 9,10-dihydroanthracene (X = Y = CH_2) and for oxanthrene (X = Y = O) seem reliable, and we decided to measure the vapor pressures at different temperatures of the other compounds, attending to the discrepancies or lack of reliable results.

Experimental Section

Materials. All of the compounds studied in this work are commercial products from Aldrich Chemical Co.: anthraquinone (X = Y = CO; CAS No. 84-65-1), anthrone (X = CO, Y = CH_2; CAS No. 90-44-8), thianthrene (X = Y = S; CAS No. 92-85-3), thioxanthone (X = CO, Y = S; CAS No. 492-22-8), and xanthone (X = CO, Y = O; CAS No. 90-47-1). The assessed purity of thianthrene was better than 97 %. The studied sample was purified by sublimation under reduced pressure followed by repeated zone melting. The final purity was assessed as being better than 99.9 % by gas chromatography (GC) performed on an Agilent 4890D gas chromatograph 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), with nitrogen as the carrier gas and an flame ionization detector. For the other four compounds studied, Aldrich certificates of analysis showed the following purities: antraquinone, 99.9 %; anthrone, 99.99 %; xanthone, 99.70 %; and thioxanthone, 98.3 %. Previously to the experimental study, samples of these four compounds were further purified by sublimation under reduced pressure. The final molar purity of these samples was assessed by differential scanning calorimetry (DSC) experiments through a fractional fusion technique[3] as being better than 99.9 %.

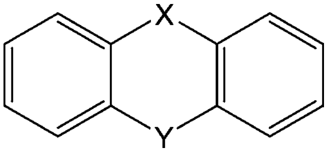
Figure 1. Structure of the molecules of the anthracene-like compound.

Differential Scanning Calorimetry. DSC was used for measuring the temperatures and enthalpies of fusion of anthraquinone, anthrone, xanthone, and thioxanthone. The experiments were carried out in hermetically sealed steel crucibles using a power-compensated differential scanning calorimeter, SETARAM model DSC 141, under a heating rate of 2 $K \cdot min^{-1}$, from 295 K up to a temperature higher than the temperature of fusion of each compound. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials: naphthalene, benzoic acid, and indium.[4] At least four independent runs were performed for each compound. Mean results and assessed experimental uncertainties (calculated as twice the standard deviations) of the temperatures of fusion, T_{fus}, (observed at the onset of the calorimetric peaks) and of the molar enthalpies of fusion, $\Delta_{cr}^{l}H_m(T_{fus})$, are presented in Table 1. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the compounds studied.

Vapor-Pressure Measurements. The vapor pressures of the compounds studied were measured at several temperatures using the Knudsen effusion technique. The vapor pressures of anthrone

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Table 1. DSC Temperatures (Onset) and Enthalpies of Fusion of the Compounds Studied

	T_{fus}/K		$\Delta_{cr}^{l}H_m(T_{fus})$/kJ·mol^{-1}	
compound	this study	literature	this study	literature
anthrone	429.5 ± 0.2	429.0[7]	22.4 ± 0.2	26.8[7]
anthraquinone	556.8 ± 0.2	555.0[8] 557.96[9]	36.30 ± 0.3	32.6[8]
thioxanthone	486.6 ± 0.4	487.8[10]	28.4 ± 0.1	35.5[10]
xanthone	448.3 ± 0.1	449.6[11]	26.6 ± 0.2	26.1[11]
thianthrene		429.58[12]		27.55[12]

Table 2. Areas and Clausing Factors of the Effusion Orifices

	orifice	A_o/mm^2	w_o[a]
small orifices	A_1	0.502	0.988
	A_2	0.499	0.988
	A_3	0.497	0.988
	D_1	0.663	0.990
medium orifices	B_4	0.774	0.991
	B_5	0.783	0.991
	B_6	0.773	0.991
	D_2	0.785	0.991
large orifices	C_7	1.116	0.992
	C_8	1.125	0.992
	C_9	1.150	0.992
	D_3	0.996	0.992

[a] $w_o = \{1 + (3l/8r)\}^{-1}$, where l is the length of the effusion orifice ($l = 0.0125$ mm) and r is its radius.

Table 3. Effusion Results for the Studied Compounds[a]

			m/mg			p/Pa		
T/K	t/s	orifices	M_S	M_M	M_L	P_S	P_M	P_L
		Thianthrene						
344.27	28927	A3−B6−C9	7.92	12.49	18.37	0.161	0.163	0.161
346.12	28927	A2−B5−C8	9.86	15.38	21.96	0.200	0.198	0.197
348.10	28927	A1−B4−C7	12.17	18.57	26.45	0.246	0.243	0.239
350.26	21574	A3−B6−C9	10.89	17.11	25.26	0.299	0.301	0.299
352.11	21574	A2−B5−C8	13.51	21.14	29.87	0.370	0.368	0.362
354.10	21574	A1−B4−C7	16.36	25.21	35.89	0.447	0.446	0.439
356.26	10173	A3−B6−C9	9.35	14.86	21.97	0.549	0.560	0.555
358.10	10173	A2−B5−C8	11.61	18.44	25.84	0.680	0.687	0.669
360.08	10173	A1−B4−C7	13.98	21.29	30.60			
360.27	10140	A3−B6−C9	13.80′	21.50	31.86			
360.17		mean of the two previous results				0.817	0.811	0.807
362.05	10140	A2−B5−C8	16.79	26.48	37.27	0.992	0.995	0.973
364.06	10140	A1−B4−C7	20.33	31.35	44.31	1.197	1.196	1.170
		Thioxanthone						
369.12	22503	A1−B4−C7	6.94	10.64	14.68	0.187	0.186	0.178
371.20	22503	A2−B5−C8	8.51	13.08	18.42	0.232	0.226	0.222
373.26	22503	A3−B6−C9	10.36	15.56	22.85	0.284	0.274	0.270
375.12	16775	A1−B4−C7	8.79	14.17	19.54	0.321	0.335	0.320
377.11	12384	A1−B4−C7	8.33	12.60	17.23	0.413	0.405	0.383
379.20	12384	A2−B5−C8	9.93	15.56	21.75	0.496	0.495	0.480
381.27	12384	A3−B6−C9	12.13	18.34	26.69	0.611	0.592	0.579
383.12	9156	A1−B4−C7	10.52	16.01	21.94	0.711	0.701	0.664
385.27	9156	A3−B6−C9	12.59	18.67	27.47	0.863	0.820	0.810
387.20	9156	A2−B5−C8	14.91	23.03	31.85	1.018	1.001	0.962
		Anthrone						
346.15	24936	D1−D2−D3	7.04	8.32	10.34	0.131	0.131	0.128
348.14	24660	D1−D2−D3	8.55	10.15	12.44	0.162	0.162	0.156
351.13	19807	D1−D2−D3	9.42	10.90	14.04	0.223	0.217	0.221
354.18	19183	D1−D2−D3	12.52	14.44	17.79	0.307	0.299	0.290
355.68	15064	D1−D2−D3	11.46	13.41	16.74	0.359	0.354	0.348
357.19	12755	D1−D2−D3	11.07	12.96	16.09	0.410	0.405	0.396
360.15	11157	D1−D2−D3	13.11	15.43	18.87	0.558	0.553	0.533
363.14	12867	D1−D2−D3	20.1	23.29	28.45	0.744	0.727	0.700
365.14	10837	D1−D2−D3	20.3	23.64	28.67	0.895	0.879	0.840
		Xanthone						
342.22	29299	A1−B4−C7	6.26	9.83	13.83	0.130	0.132	0.129
344.15	29299	A2−B5−C8	7.77	12.03	16.94	0.163	0.160	0.157
346.26	29299	A3−B6−C9	9.34	14.82	21.62	0.197	0.201	0.196
348.26	21908	A3−B6−C9	8.66	13.14	19.73	0.245	0.238	0.240
350.26	16634	A3−B6−C9	8.04	12.64	18.31	0.301	0.303	0.295
352.12	16634	A2−B5−C8	9.89	15.19	21.36			
352.12	21908	A2−B5−C8	13.08	19.94	28.26			
352.12		mean of the two previous results				0.370	0.360	0.354
354.20	16634	A1−B4−C7	12.13	18.78	26.03	0.451	0.452	0.434
356.21	21908	A1−B4−C7	19.52	29.76	41.65	0.553	0.546	0.529
358.26	10822	A3−B6−C9	11.60	17.89	26.29	0.674	0.667	0.658
360.15	10822	A2−B5−C8	14.04	21.66	30.47	0.814	0.799	0.781
362.22	10822	A1−B4−C7	17.11	26.41	36.81	0.989	0.989	0.954
		Anthraquinone						
377.06	25682	A1−C7	7.16		15.18	0.173		0.164
379.08	25682	A2−C8	8.62		18.64	0.210		0.200
381.26	25682	A3−C9	10.18		23.27	0.250		0.246
383.26	17576	A3−C9	8.32		19.55	0.299		0.302
385.26	16312	A3−C9	9.24		21.08	0.359		0.352
386.89	17576	A2−C8	12.12		26.89			
387.06	16312	A2−C8	11.19		24.00			
386.98		mean of the two previous results				0.434		0.419
389.01	16312	A1−C7	13.44		28.12			
389.03	17576	A1−C7	14.78		31.32			
389.22		mean of the two previous results				0.524		0.495
391.26	12808	A3−C9	12.17		28.83			0.618
393.08	12808	A2−C8	14.96		32.61	0.743		0.716
395.03	12808	A1−C7	17.89		38.31	0.886		

[a] Results related to the small (A1, A2, A3, D1), medium (B4, B5, B6, D2), and large (C7, C8, C9, D3) effusion orifices are denoted, respectively, by the subscripts S, M, and L.

were measured using a Knudsen effusion apparatus enabling the simultaneous operation of three different effusion cells, previously described in detail.[5] A few changes have been introduced since 2001 to the original apparatus design and to the lids of the effusion cells, when the previous effusion orifices made in brass foil were replaced by more precise orifices made in very thin platinum foil. In a typical effusion experiment the mass loss, Δm, of the samples during a convenient effusion time period, t, is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period in a system evacuated to a pressure near $1 \cdot 10^{-4}$ Pa. The samples are assumed to be in thermal equilibrium with a thermostatically controlled silicone oil bath where glass tubes containing the effusion cells are immersed. The temperature of the bath is measured using Amarell mercury thermometers, calibrated by Eichamt Wertheim (Germany), and graduated to 0.01 K. The vapor pressures of the other four compounds were measured using a Knudsen effusion apparatus enabling the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks. The detailed description of this apparatus and the results obtained by measuring vapor pressures of reference crystalline compounds were previously published.[6] During an effusion experiment, each aluminum block is kept at a constant temperature (different from the temperature of the other two blocks) and contains three effusion cells with effusion orifices of different areas: one "*small*" ($A_o \approx 0.5$ mm^2: series A), one "*medium*" ($A_o \approx 0.8$ mm^2: series B), and one "*large*" ($A_o \approx 1.1$ mm^2: series C). The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 DIN (in a four-wire connection) previously calibrated by comparison with a standard platinum resistance thermometer (25 Ω; Tinsley, 5187A). For both apparatuses the measured pressure at the temperature T of the experiment is calculated using eq 1

$$p = (m/A_o w_o t)(2\pi RT/M)^{1/2} \qquad (1)$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_o is the area of the effusion orifice, and w_o is

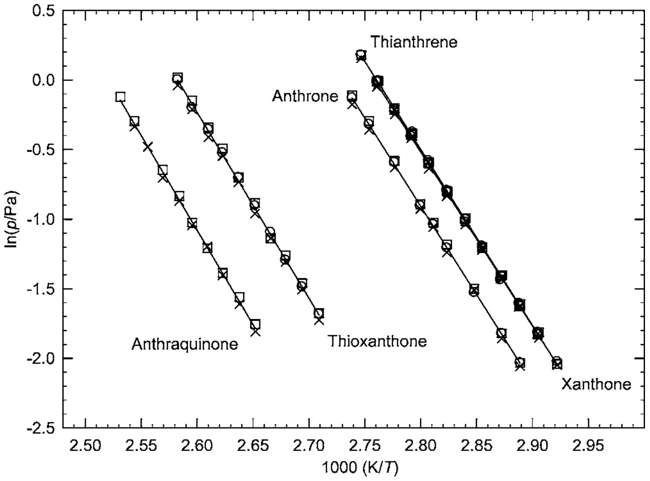

Figure 2. Plots of ln *p* against 1/*T* for the compounds studied. □, small effusion orifices; ○, medium effusion orifices; ×, large effusion orifices.

the respective Clausing factor. The uncertainty of the measured pressures and temperatures is estimated to be better than ± 0.02 Pa and ± 0.01 K, respectively. The exact areas and Clausing factors of each used effusion orifice, made in platinum foil of 0.0125 mm thickness, are presented in Table 2.

Results and Discussion

The measured vapor pressures related to each effusion cell at each temperature, for each studied compound, are presented in Table 3. The plots of ln(*p*/Pa) versus 1/*T* are shown in Figure 2 where, due to similar volatility, the results for thianthrene and xanthone are fitted by two straight lines that hardly can be distinguished. Table 4 presents for the three series of effusion orifices the detailed parameters of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(\text{K}/T)$, where *a* is a constant and $b = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)/R$, and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T\rangle$. Because of the lack of enough purified sample of anthraquinone, only six effusion cells were used in the study of this compound. The values of the standard molar enthalpy and Gibbs energy of sublimation at the reference temperature $\theta = 298.15$ K were derived by fitting the experimental results of the vapor pressures by the truncated form of Clarke and Glew equation (eq 2),[13]

$$R\ln\left(\frac{p}{p^{\text{o}}}\right) = -\frac{\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(\theta)}{\theta} + \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (2)$$

where *p* is the vapor pressure at the temperature *T*, p^0 is a selected reference pressure ($p^{\text{o}} = 10^5$ Pa in this work), *R* is the molar gas constant, and $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the crystalline phase. The values of $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}(\theta)$ inputted in eq 2 are presented in Table 6. Some of these values were calculated from values of $C_{p,\text{m}}^{\text{o}}(\text{g})$ using eq 3[14] which is a rearrangement of eq 4 proposed by Chickos et al.[15]

$$\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}(\theta)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -\{0.9 + 0.176C_{p,\text{m}}^{\text{o}}(\text{g})\} \quad (3)$$

$$\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}(\theta)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -\{0.75 + 0.15C_{p,\text{m}}^{\text{o}}(\text{cr})\} \quad (4)$$

Some of the $C_{p,\text{m}}^{\text{o}}(\text{g})$ values inserted in eq 3 were calculated using density functional theory (DFT) with the hybrid exchange

Table 4. Experimental Results for the Sublimation of the Compounds Studied[a]

effusion orifices	*a*	*b*	$\langle T\rangle$/K	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)$/kJ·mol⁻¹	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K)/kJ·mol⁻¹	$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}$(298.15 K)/kJ·mol⁻¹	R^2
			Anthraquinone				
A	34.26 ± 0.34	13584 ± 133		112.9 ± 1.1	116.1 ± 1.1	56.95 ± 0.26	0.9992
C	34.19 ± 0.37	13570 ± 142		112.8 ± 1.2	115.9 ± 1.2	56.99 ± 0.27	0.9992
mean	34.22 ± 0.50	13577 ± 194	386.04	112.8 ± 1.6	116.0 ± 1.6	57.0 ± 0.4	
			Anthrone				
D1	34.98 ± 0.14	12811 ± 55		106.5 ± 0.5	108.6 ± 0.5	48.51 ± 0.06	0.9999
D2	34.71 ± 0.19	12719 ± 66		105.8 ± 0.5	107.8 ± 0.5	48.42 ± 0.09	0.9998
D3	34.22 ± 0.31	12554 ± 109		104.4 ± 0.9	106.4 ± 0.9	48.27 ± 0.14	0.9995
mean	34.64 ± 0.26	12695 ± 93	355.54	105.6 ± 0.8	107.6 ± 0.8	48.4 ± 0.1	
			Thianthrene				
A	34.92 ± 0.20	12649 ± 73		105.2 ± 0.6	106.5 ± 0.6	47.24 ± 0.10	0.9997
B	34.98 ± 0.18	12670 ± 64		105.3 ± 0.5	106.6 ± 0.5	47.23 ± 0.08	0.9998
C	34.79 ± 0.13	12605 ± 45		104.8 ± 0.4	106.1 ± 0.4	47.22 ± 0.06	0.9999
mean	34.90 ± 0.20	12641 ± 71	354.16	105.1 ± 0.6	106.4 ± 0.6	47.2 ± 0.1	
			Thioxanthone				
A	34.78 ± 0.41	13454 ± 153		111.9 ± 1.3	114.8 ± 1.3	54.53 ± 0.27	0.9990
B	34.33 ± 0.32	13291 ± 120		110.5 ± 1.0	113.4 ± 1.0	54.28 ± 0.21	0.9994
C	34.27 ± 0.28	13283 ± 104		110.4 ± 0.9	113.3 ± 0.9	54.35 ± 0.18	0.9995
mean	34.46 ± 0.40	13343 ± 147	378.16	110.9 ± 1.2	113.8 ± 1.2	54.4 ± 0.3	
			Xanthone				
A	34.71 ± 0.15	12576 ± 55		104.6 ± 0.5	106.4 ± 0.5	47.21 ± 0.07	0.9998
B	34.48 ± 0.22	12496 ± 77		103.9 ± 0.6	105.8 ± 0.6	47.12 ± 0.10	0.9997
C	34.23 ± 0.10	12418 ± 35		103.2 ± 0.3	105.1 ± 0.3	47.08 ± 0.05	0.9999
mean	34.47 ± 0.18	12497 ± 67	352.22	103.9 ± 0.6	105.8 ± 0.6	47.1 ± 0.1	

[a] Experimental uncertainties of the selected values (mean values) were calculated as twice the standard deviation; *a* and *b* are from Clausius−Clapeyron equation $\ln(p/\text{Pa}) = a - b(\text{K}/T)$, where $b = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)/R$; the values of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K) and of $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}$(298.15 K) were derived from Clarke Glew eq 2 considering the reference pressure $p^{\text{o}} = 0.1$ MPa.

Table 5. Literature Results for Standard Molar Enthalpy and Gibbs Energy of Sublimation of the Compounds Studied

	$\Delta^{r}_{cr}H^{o}_{m}$(298.15 K)	$\Delta^{r}_{cr}G^{o}_{m}$(298.15 K)		
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	method	ref
anthraquinone	108.0[a]	50.0[a]	ME	21
	135 ± 3[a]		DSC	22
	112.3 ± 0.8[a]	55.9[a]	ME	23
	113.1 ± 0.8		Cal	23
	112.3 ± 0.2[a]		Cal	24
	117.8 ± 5.0[a]	58.3[a]	ME	20
	116.0 ± 1.6	57.0 ± 0.4	ME	this study
anthrone	103.7 ± 0.6		Cal	25
	106.1 ± 0.8[a]	47.5[a]	GS	19
	107.6 ± 0.8	48.4 ± 0.1	ME	this study
thianthrene	101.8[a]	46.2[a]	GS	26
	104.3[a]	46.9[a]	IP	18
	99.9 ± 0.5[a]		Cal	27
	106.4 ± 0.6	47.2 ± 0.1	ME	this study
thioxanthone	114.8 ± 0.4[a]		Cal	10
	113.8 ± 1.2	54.4 ± 0.3	ME	this study
xanthone	98.6 ± 0.4[a]		Cal	11
	105.8 ± 0.6	47.1 ± 0.1	ME	this study

[a] Calculated in this work from the literature results, using $\Delta^{g}_{cr}C^{o}_{p,m}$ values presented in Table 6; ME, mass-loss Knudsen effusion; DSC, differential scanning calorimetry; Cal, calorimetry; GS, gas saturation; IP, inclined piston manometer.

correlation functional B3LYP at the 6-311++G(d,p) level of theory. The frequencies were scaled using the scale factor of 0.9688,[16] and the Gaussian 03 software package[17] was used for the necessary computational calculations.

Table 5 presents literature values for $\Delta^{g}_{cr}H^{o}_{m}$ (298.15 K) and for $\Delta^{g}_{cr}G^{o}_{m}$(298.15 K) for the compounds studied. To the best of our knowledge, the present results for vapor pressures of crystalline xanthone and thioxanthone are the first ones to be published. The calorimetric enthalpies of sublimation determined by Sabbah and El Watik are similar to our result for thioxanthone[10] but in considerable disagreement for xanthone.[11] For the other three compounds studied there are several literature results, most of them in disagreement with the results derived in the present study with the exceptions of the values derived by Steele et al.[18] for thianthrene (although those results were based on vapor pressures measured at only four different temperatures) and of the values derived by Verevkin[19] for anthrone. The recently published value by Goldfarb and Suuberg[20] for the enthalpy of sublimation of anthraquinone also agrees with the result derived in this work, inside the very large uncertainty assigned by those authors to their result.

The main purpose of this study was to develop a scheme for predicting the vapor pressures and enthalpies of sublimation of anthracene-like compounds. So we estimated the contribution of the different meso substituents in the positions X and Y of the general structure presented in Figure 1 using a multivariable linear regression analysis over the variables N(O), N(S), N(CO), and $N(CH_2)$, where N represents the number of each type of X and Y substituent present in the structural formula of each compound. The regressions were anchored in the values for naphthalene presented in Table 6, for which the number of meso substituents was considered zero. As anthracene was the only compound containing CH groups in positions X and Y, the coefficients of CH groups were calculated dividing by two the differences in the standard molar enthalpy and Gibbs energy of sublimation between anthracene and naphthalene. The estimation of the enthalpy of sublimation for anthracene-like compounds is described by eq 5 with a standard deviation $\sigma = 1.3\ kJ \cdot mol^{-1}$, while eq 6 represents the estimation of the standard Gibbs energy of sublimation with a standard deviation $\sigma = 0.9\ kJ \cdot mol^{-1}$. The vapor pressure at the temperature 298.15 K, $p(T = 298.15\ K)$, may be calculated by eq 8, derived from eq 6, using the well-known thermodynamic relation represented by eq 7.

$$\Delta^{g}_{cr}H^{o}_{m}(298.15\ K)/kJ \cdot mol^{-1} = 72.7 + 13.75N(CH) + 9.95N(O) + 17.16N(S) + 22.48N(CO) + 11.23N(CH_2) \qquad (R^2 = 0.994) \quad (5)$$

$$\Delta^{g}_{cr}G^{o}_{m}(298.15\ K)/kJ \cdot mol^{-1} = 22.6 + 11.50N(CH) + 6.60N(O) + 12.60N(S) + 17.76N(CO) + 7.36N(CH_2) \qquad (R^2 = 0.995) \quad (6)$$

$$\Delta^{g}_{cr}G^{o}_{m}(298.15\ K) = -298.15R\ \ln\{p(T = 298.15\ K)/10^5\} \quad (7)$$

$$\ln\{p(T = 298.15\ K)/Pa\} = 2.39 - 4.64N(CH) - 2.66N(O) - 5.08N(S) - 7.16N(CO) - 2.97N(CH_2) \quad (8)$$

Results of $\Delta^{g}_{cr}H^{o}_{m}$(298.15 K) and $\Delta^{g}_{cr}G^{o}_{m}$(298.15 K) for phenoxathiin were not considered when deriving the correlations described by eqs 5 and 6, respectively. These correlations are graphically represented in Figures 3 and 4 where it is easily noticed that the values for phenoxathiin are not well-fitted by those correlations, while for all of the other compounds the fittings may be considered very good. The reason for this behavior of phenoxathiin results is not obvious, but it seems to

Table 6. Results of Standard Molar Enthalpy, Gibbs Energy, and Entropy of Sublimation at the Temperature 298.15 K

			$C^{o}_{p,m}$(g)	$\Delta^{g}_{cr}C^{o}_{p,m}$	$\Delta^{r}_{cr}H^{o}_{m}$(exp)	$\Delta^{r}_{cr}H^{o}_{m}$(eq 5)	$\Delta^{r}_{cr}G^{o}_{m}$(exp)	$\Delta^{r}_{cr}G^{o}_{m}$(eq 6)	$\Delta^{r}_{cr}G^{o}_{m}$(eq 9)	$\Delta^{g}_{cr}S^{o}_{m}$
compound	X	Y	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
anthraquinone	C=O	C=O	197.8[a]	−35.7[b]	116.0 ± 1.6[c]	117.7	57.0 ± 0.4[c]	58.1	57.8	198
anthrone	C=O	CH_2	199.7[c]	−36[b]	107.6 ± 0.8[c]	106.4	48.4 ± 0.1[c]	47.7	47.6	199
thianthrene	S	S	197.0[c]	−23.1[d]	106.4 ± 0.6[c]	107.0	47.2 ± 0.1[c]	47.8	46.8	198
thioxanthone	S	C=O	200.9[c]	−36.3[b]	113.8 ± 1.2[c]	112.3	54.4 ± 0.3[c]	53.0	53.7	199
xanthone	O	C=O	193.0[c]	−34.9[b]	105.8 ± 0.6[c]	105.1	47.1 ± 0.1[c]	47.0	47.1	197
xanthene	O	CH_2			92.6 ± 0.1[e]	93.9	36.21 ± 0.01[e]	36.6	35.8	189
tioxanthene	S	CH_2	194.8[f]	−35.2[b]	100.9 ± 0.2[f]	101.1	42.12 ± 0.04[f]	42.6	42.2	197
phenoxathiin	O	S			96.9 ± 0.4[e]	99.8	36.53 ± 0.03[e]	41.5	36.9	203
9,10-dihydroanthracene	CH_2	CH_2			95.3 ± 0.2[g]	95.2	37.4 ± 0.4[g]	37.3	36.8	194
oxanthrene	O	O	180.2[h]	−32.6[b]	92.9[i]	92.6	35.9[i]	35.8	35.8	191
anthracene	CH	CH			100.2 ± 0.4[j]	100.2	45.6 ± 0.3[j]	45.6	45.1	183
naphthalene					72.70 ± 0.04[k]	72.7	22.58 ± 0.01[k]	22.6	22.2	168

[a] Ref 28. [b] Calculated from $C^{o}_{p,m}$(g) using eq 3. [c] This work. [d] Calculated from the difference between $C^{o}_{p,m}(g) = 197.0\ J \cdot K^{-1} \cdot mol^{-1}$ and the value $C^{o}_{p,m}(cr) = 220.1\ J \cdot K^{-1} \cdot mol^{-1}$ from ref 18. [e] Ref 1. [f] Ref 2. [g] Ref 29. [h] Ref 30. [i] calculated in the present work from the experimental results presented in ref 31 using $\Delta^{g}_{cr}C^{o}_{p,m} = -32.6\ J \cdot K^{-1} \cdot mol^{-1}$; [j] Ref 5. [k] Ref 32.

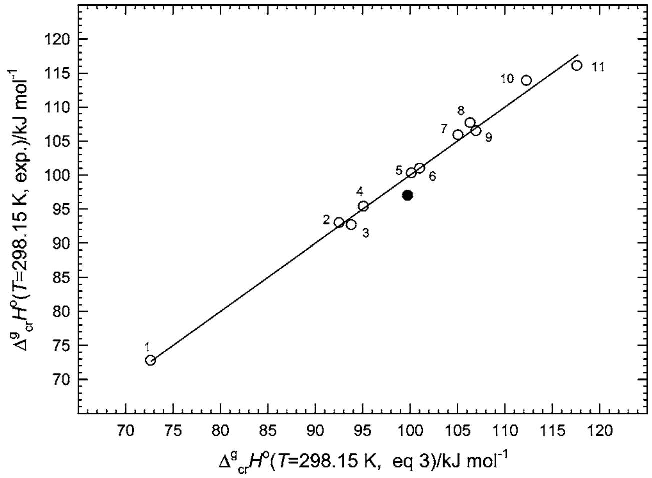

Figure 3. Plot of calculated values (eq 5) of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) against experimental values. 1, naphthalene; 2, oxanthrene; 3, xanthene; 4, 9,10-dihydroanthracene; 5, anthracene; 6, thioxanthene; 7, xanthone; 8, anthrone; 9, thianthrene; 10, thioxanthone; 11, anthraquinone; ●, phenoxathiin (not included in the correlation).

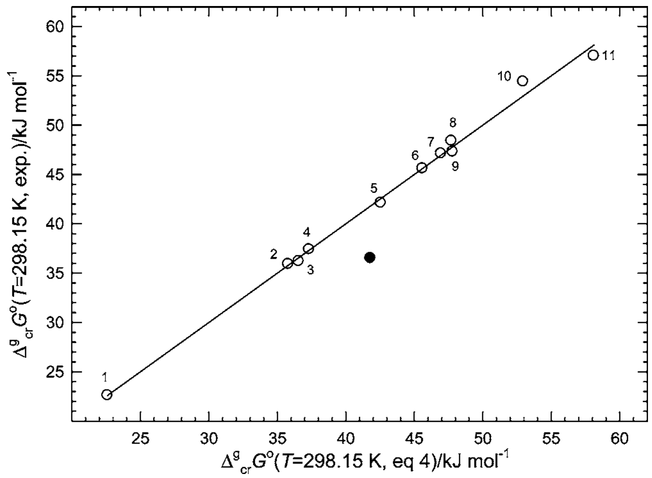

Figure 4. Plot of calculated values (eq 6) of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) against experimental values. 1, naphthalene; 2, oxanthrene; 3, xanthene; 4, 9,10-dihydroanthracene; 5, thioxanthene; 6, anthracene; 7, xanthone; 8, anthrone; 9, thianthrene; 10, thioxanthone; 11, anthraquinone; ●, phenoxathiin (not included in the correlation).

be connected with its singular crystalline packing features induced by the strong difference between the angles around the oxygen atom (C—O—C) and around the sulfur atom (C—S—C) reported as 117.4° and 97.7°, respectively.[33] As can be noticed in Table 6 and in Figure 5, the entropy of sublimation of the anthracene-like compounds {calculated as [$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) − $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)]/298.15} grows slightly with the enthalpy of sublimation, but for phenoxathiin the value of the entropy of sublimation is significantly higher than would be expected from its value of enthalpy of sublimation. So it seems that the packing arrangement of crystalline phenoxathiin either affects the intensity of the intermolecular forces (diminishing the enthalpy of sublimation) or lowers the entropy of the molecules in the crystalline packing or both.

In previous works from our research group, correlations between enthalpies of sublimation and temperature of sublimation at a reference pressure were derived for families of several compounds (hydroxyquinolines,[34] quinoxalines,[35] carboxylic acids[36−39]). Recently, similar correlations have been derived between $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)[40,41] for several substitued benzenedicarboxylates and for

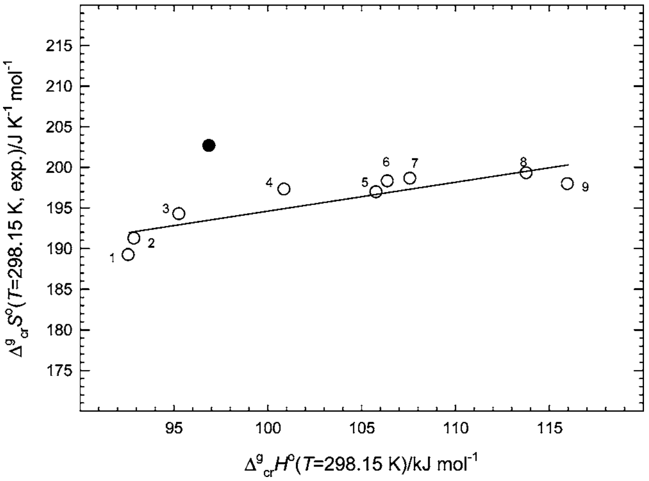

Figure 5. Plot of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) against $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) experimental values. 1, xanthene; 2, oxanthrene; 3, 9,10-dihydroanthracene; 4, thioxanthene; 5, xanthone; 6, thianthrene; 7, anthrone; 8, thioxanthone; 9, anthraquinone; ●, phenoxathiin (not included in the correlation).

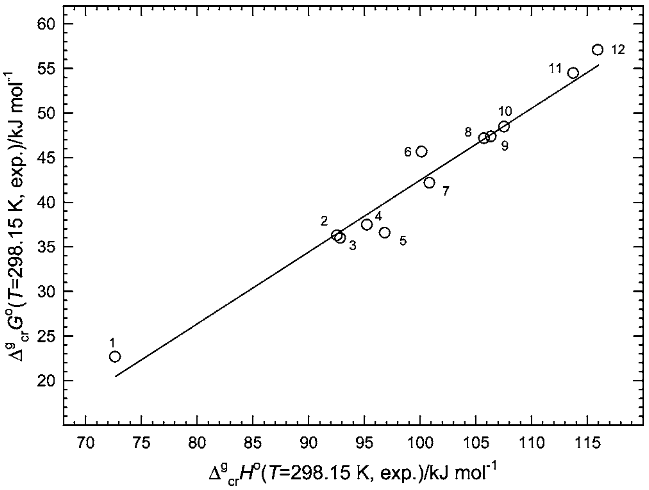

Figure 6. Plot of experimental values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) against experimental values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K). 1, naphthalene; 2, xanthene; 3, oxanthrene; 4, 9,10-dihydroanthr-acene; 5, phenoxathiin; 6, anthracene; 7, thioxanthene; 8, xanthone; 9, thianthrene; 10, anthrone; 11, thioxanthone; 12, anthraquinone.

para-benzoic acids, and it was observed that the quality of such correlations is significantly enhanced when the temperature of fusion of the several *para*-benzoic acids was also considered as independent variable.[41] Figure 6 shows the graphic representation of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = f\{\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\}$. The correlation between these two variables is not very good ($R^2 = 0.967$), but by correlating the three thermodynamic parameters {$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), and T_{fusion}} for the 12 compounds presented in Table 6, an excellent correlation represented by eq 9 is derived, as may be observed in Figure 7. This equation enables the estimation of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) for all of the considered compounds (including phenoxathiin), with a standard deviation $\sigma = 0.6$ kJ·mol^{-1}. Combining eq 9 with eq 7, eq 10 is obtained, enabling the determination of the vapor pressure at $T =$ 298.15 K of the 12 compounds with an excellent accuracy.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = -38.1 + 0.645\ \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) + 0.038T_{\mathrm{fusion}} \qquad (R^2 = 0.996) \tag{9}$$

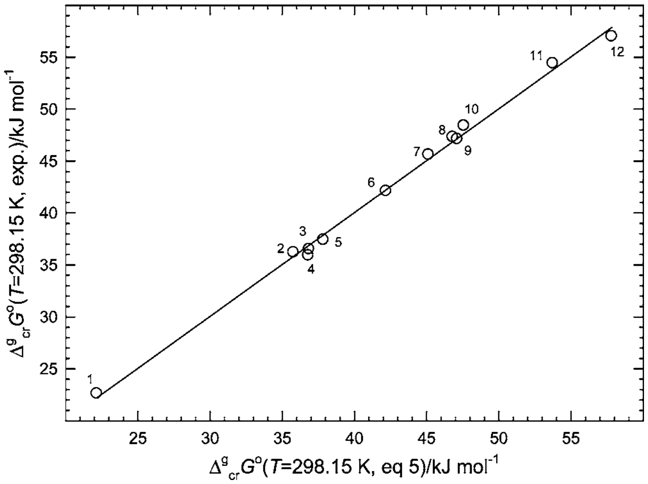

Figure 7. Plot of calculated values (eq 9) of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) against experimental values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$(298.15 K). 1, naphthalene; 2, xanthene; 3, phenoxathiin; 4, oxanthrene; 9,10-dihydroanthracene; 5, 9,10-dihydroanthracene; 6, thioxanthene; 7, anthracene; 8, thianthrene; 9, xanthone; 10, anthrone; 11, thioxanthone; 12, anthraquinone.

$$\ln\{p(T = 298.15\ \mathrm{K})/\mathrm{Pa}\} = 26.87 - 0.260\{\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}\} - 0.0153(T_{\mathrm{fusion}}/\mathrm{K}) \quad (10)$$

Besides the values of temperature of fusion determined in the present work and the literature value for thianthrene presented in Table 1, the following values were used when deriving eq 9: xanthene, $T_{\mathrm{fusion}} = 373.7$ K;[42] thioxanthene, $T_{\mathrm{fusion}} = 401.7$ K;[42] phenoxathiin, $T_{\mathrm{fusion}} = 328.8$ K;[12] 9,10-dihydroanthracene, $T_{\mathrm{fusion}} = 382.15$ K;[43] oxanthrene, $T_{\mathrm{fusion}} = 395.7$ K;[31] anthracene, $T_{\mathrm{fusion}} = 491.2$ K;[44] and naphthalene, $T_{\mathrm{fusion}} = 353.2$ K.[44]

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