

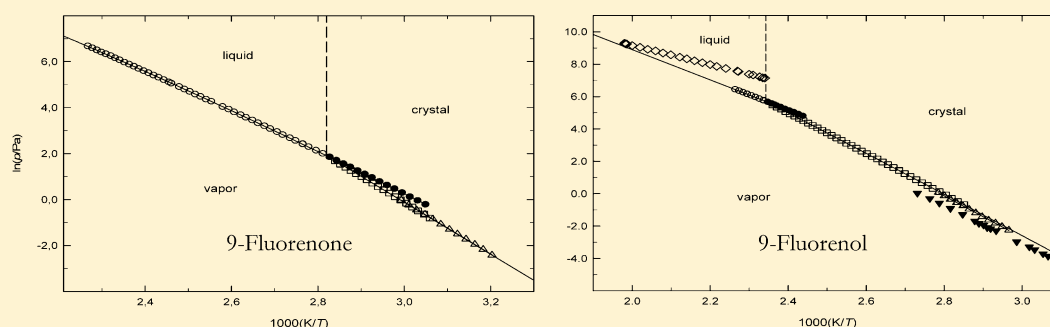
Experimental and Computational Study of the Thermodynamic Properties of 9-Fluorenone and 9-Fluorenol

Manuel J. S. Monte,^{*,†} Rafael Notario,[‡] Maria M. G. Calvino,[†] Ana R. R. P. Almeida,[†] Luísa M. P. F. Amaral,[†] Ana I. M. C. Lobo Ferreira,[†] and Maria D. M. C. Ribeiro da Silva[†]

[†]Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal

[‡]Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain

S Supporting Information



ABSTRACT: This report presents a study of the thermodynamic properties of 9-fluorenone and 9-fluorenol. The standard enthalpies of formation of 9-fluorenone and 9-fluorenol in the crystalline phase at $T = 298.15$ K were determined from the energies of combustion in oxygen as $-(11.4 \pm 3.8)$ kJ·mol⁻¹ and $-(66.3 \pm 2.9)$ kJ·mol⁻¹, respectively. Vapor pressures of the two compounds were measured at several temperatures using two different experimental methods (Knudsen effusion for crystalline-phase vapor pressures and a static method for crystalline- and liquid-phase vapor pressures), which yielded reliable values of the enthalpies of sublimation, vaporization, and fusion. The sublimation and fusion enthalpies were also determined using calorimetric methods. The enthalpies of sublimation at $T = 298.15$ K were derived from the static vapor pressure measurements as (95.1 ± 0.5) kJ·mol⁻¹ for 9-fluorenone and (108.3 ± 0.5) kJ·mol⁻¹ for 9-fluorenol. The results enabled the determination of the standard Gibbs energy of the aerobic reactions of oxidation of fluorene to 9-fluorenone and 9-fluorenone and of the oxidation of 9-fluorenol to 9-fluorenone. Values of the standard enthalpies of formation in the gas phase were also calculated.

INTRODUCTION

Fluorene and 9-fluorenone are important building blocks and intermediates in organic synthesis and materials chemistry with a large number of applications ranging from the synthesis of medicinal and pharmaceutical agents, organic dyes, and plastic additives to the preparation of organic light-emitting diodes.¹ This report presents an extended experimental and computational thermodynamic study of 9-fluorenone and 9-fluorenol (Figure 1), which was undertaken in order to evaluate the energetic and structural effects inherent in the presence of the ketone and hydroxyl functional groups at the 9-position of the

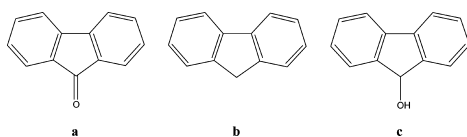


Figure 1. Structural formulas of (a) 9-fluorenone, (b) fluorene, and (c) 9-fluorenol.

fluorene structure. As both of these compounds may appear as a result of aerobic oxidation of fluorene, one of our goals was to combine the thermodynamic parameters determined in this work with the ones determined previously for fluorene² to calculate the standard Gibbs energies of these oxidation reactions. This knowledge may be important for studies concerning applications of compounds with a fluorene or 9-fluorenone core in commercial displays. The oxidation of fluorene to 9-fluorenone, besides being the main process for preparing the latter compound,¹ is also suspected to be responsible for the unwanted change in color due to the emergence of a low-energy green emission peak in the blue-light emission of fluorene–fluorenone copolymers.³ Knowledge of the volatility properties of these compounds would also be relevant, as a typical way of obtaining thin films of the emitting

Received: April 30, 2012

Accepted: August 2, 2012

Published: August 15, 2012

materials is through vacuum deposition on appropriate substrates.^{4,5}

For 9-fluorenone, two published values exist for the enthalpy of formation in the crystalline phase, $-(36.1 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ ⁶ and $-(7.71 \pm 0.71) \text{ kJ}\cdot\text{mol}^{-1}$,⁷ while values for the enthalpy of sublimation at $T = 298.15 \text{ K}$, $\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}(298.15 \text{ K})$, range from $(88.4 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ ⁶ to $(93.0 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$.⁸ For 9-fluorenol, we could not find any literature results for the enthalpy of formation, but there are published data for sublimation vapor pressures,⁹ from which we calculated $\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (99.5 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$. Collecting consistent results for the physicochemical properties of organic compounds presenting a fluorene or 9-fluorenone core is one of our recent interests.^{2,10} After establishing a solid basis of reliable results for these compounds, we will extend this study to several derivatives in order to develop well-supported schemes that can be used to predict crystalline-phase and gas-phase thermodynamic properties.

EXPERIMENTAL SECTION

Materials and Purity Control. 9-Fluorenone (CAS no. 486-25-9) and 9-fluorenol (CAS no. 1689-64-1) were commercially obtained and sublimed under reduced pressure before the experimental measurements. The purities of the purified samples were verified by gas chromatography using an Agilent 4890D gas chromatograph equipped with an HP-5 column (0.05 diphenyl and 0.95 dimethylpolysiloxane by mole fraction) and a flame ionization detector. Nitrogen was used as the carrier gas. The initial and final purities of the samples as determined by gas chromatography are presented in Table 1.

Table 1. Source, Purification, and Analysis Details of the Studied Samples

chemical name	source	minimum initial mass fraction purity	purification method	final mass fraction purity	analysis method
9-fluorenone	Sigma-Aldrich	0.98	sublimation	0.9999	GC ^a
9-fluorenol	Alfa Aesar	0.98	sublimation	0.9998	GC ^a

^aGC = gas chromatography.

Comparison of the mass of carbon dioxide collected in the combustion experiments with that calculated from the mass of the sample also confirmed the purity of the samples. The average ratios and specific densities, respectively, are (1.0002 ± 0.0004) and $1.24 \text{ g}\cdot\text{cm}^{-3}$ for 9-fluorenone¹¹ and (0.9999 ± 0.0005) and $1.13 \text{ g}\cdot\text{cm}^{-3}$ for 9-fluorenol,¹² where the uncertainties are twice the standard deviation of the mean. IUPAC-recommended relative atomic masses¹³ were used in all molar mass calculations.

Differential Scanning Calorimetry Analysis. Temperatures and enthalpies of fusion and the thermal behavior of the purified samples were determined using differential scanning calorimetry (DSC) using a Setaram DSC 141 calorimeter. High-purity indium (mass fraction > 0.99999) was used to calibrate the power scale of the calorimeter, and its temperature scale was calibrated by determining the temperatures (onset points) of fusion, T_{fus} , of four high-purity materials recommended as standards:¹⁴ naphthalene, benzoic acid, tin, and indium. For each compound, four or five runs using fresh

samples were performed at a heating rate of $3.3\cdot 10^{-2} \text{ K}\cdot\text{s}^{-1}$. The T_{fus} values and the enthalpies of fusion, $\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}(T_{\text{fus}})$, were calculated from the DSC thermograms, with uncertainties assigned as the standard deviation of the mean.

Static Bomb Combustion Calorimetry. The combustion experiments were conducted in a static bomb calorimeter equipped with a twin-valve bomb with an internal volume of 0.290 dm^3 .^{15–17} In each experiment, 1.00 cm^3 of deionized water was placed into the bomb, and the crystalline sample pellet was subjected to ignition at $T = (298.150 \pm 0.001) \text{ K}$ under an oxygen atmosphere at $p = 3.04 \text{ MPa}$ according to the method described by Coops et al.¹⁸ The mass of each compound pellet, $m(\text{cpd})$, was corrected by considering the mass of carbon dioxide produced during the combustion, $m(\text{CO}_2, \text{ total})$, and taking into account the quantity formed from the combustion of the cotton thread.

The determination of the energy equivalent of the calorimeter, $\epsilon(\text{calor})$, was performed using benzoic acid (CAS no. 65-85-0, NIST standard reference material SRM 39j), which has a massic energy of combustion of $-(26434 \pm 3) \text{ J}\cdot\text{g}^{-1}$ under similar experimental conditions. From eight calibration experiments, $\epsilon(\text{calor})$ was determined to be $(15551.7 \pm 1.2) \text{ J}\cdot\text{K}^{-1}$, where the uncertainty is the standard deviation of the mean. An average mass of 2900.0 g of water was added to the calorimeter, and readings of its temperature were taken at intervals of 10 s using a four-wire calibrated ultrastable thermistor probe (Thermometrics, standard serial no. 1030) with a precision of $\pm 1\cdot 10^{-4} \text{ K}$. Data acquisition, control of the calorimeter temperature, and the calculation of the adiabatic temperature change were achieved using the software program LABTERMO.^{19,20} The value $\Delta_{\text{cr}}^{\circ}U = -16240 \text{ J}\cdot\text{g}^{-1}$ was used for the energy of combustion of the cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$.²¹ The nitric acid produced during the experiments was determined by volumetry, and the corrections for its formation were performed using the standard energy of formation value $\Delta_{\text{f}}^{\circ}U_{\text{m}}^{\circ}(\text{HNO}_3, \text{ aq}, 0.1 \text{ mol}\cdot\text{dm}^{-3}) = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$.²² The value $(\partial u/\partial p)_T = -0.2 \text{ J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$ at $T = 298.15 \text{ K}$ ²³ was assumed, and the standard massic energy of combustion, $\Delta_{\text{cr}}^{\circ}u^{\circ}$, was calculated using the procedure given by Hubbard et al.²⁴

Calvet Microcalorimetry Measurements. A Calvet microcalorimeter (Setaram model HT 1000) was used to determine the standard molar enthalpy of sublimation of 9-fluorenone following the previously described vacuum sublimation drop-microcalorimetry technique.^{25,26} The microcalorimeter was calibrated using naphthalene (Aldrich, mass fraction purity > 0.99) and the literature value $\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (72.60 \pm 0.60) \text{ kJ}\cdot\text{mol}^{-1}$.²⁷ From five independent experiments, the calibration constant of the calorimeter at the experimental temperature was determined to be $k(T = 367.7 \text{ K}) = (0.9965 \pm 0.0030)$, where the uncertainty is twice the standard deviation of the mean. In each experiment, at the chosen temperature T , a thin glass capillary tube sealed at one end and filled with (3 to 5) mg of the crystalline sample was dropped into the reaction cell at the same time that a blank capillary tube was dropped into the reference cell. Thermal corrections due to the slightly different masses of the sample and reference capillary tubes as well as to the different sensitivities of the calorimeter cells were applied after separate blank-correction experiments were performed.

Vapor Pressure Measurements. The vapor pressures of crystalline and liquid 9-fluorenone and 9-fluorenol were measured at different temperatures using a static method.²⁸

Table 2. Values of Standard ($p^\circ = 0.1$ MPa) Massic and Molar Energies of Combustion, Molar Enthalpies of Combustion, and Molar Enthalpies of Formation of 9-Fluorenone and 9-Fluorenone in Their Crystalline Phases at $T = 298.15$ K^a

compound	$\langle \Delta_c u^\circ \rangle$	$\Delta_c U_m^\circ(\text{cr})$	$\Delta_c H_m^\circ(\text{cr})$	$\Delta_f H_m^\circ(\text{cr})$
	J·g ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹
9- fluorenone	-34648.0 ± 9.0	-6243.8 ± 3.4	-6247.5 ± 3.4	-11.4 ± 3.8
9- fluorenone	-35525.7 ± 5.2	-6473.5 ± 2.3	-6478.5 ± 2.3	-66.3 ± 2.9

^aEach uncertainty is twice the overall standard deviation of the mean of the values derived in each combustion experiment and includes the uncertainties in calibration.

Table 3. Vapor Pressure Results for 9-Fluorenone^a

T	p		T	p		T	p	
K	Pa	100Δp/p ^b	K	Pa	100Δp/p ^b	K	Pa	100Δp/p ^b
Crystalline Phase (Knudsen Effusion) ^c								
312.19	0.089	-1.1	320.20	0.225	0.6	328.11	0.528	0.8
314.21	0.115	0.5	322.11	0.273	-0.9	330.18	0.638	-1.8
316.11	0.143	0.7	324.19	0.344	-0.5	332.18	0.796	-0.2
318.18	0.180	0.5	326.19	0.430	0.6	334.10	0.977	0.9
Crystalline Phase (Static)								
326.88	0.45	-0.8	335.78	1.13	-0.5	344.68	2.72	0.6
328.32	0.53	0.3	337.25	1.33	1.1	346.20	3.11	-0.4
329.83	0.61	-1.4	338.75	1.53	0.3	347.68	3.55	-1.0
331.30	0.72	-0.1	340.21	1.77	0.6	349.17	4.09	-0.7
332.81	0.85	1.0	341.69	2.05	0.9	350.65	4.67	-1.0
334.29	0.98	0.2	343.19	2.35	0.1	352.14	5.44	0.7
Liquid Phase								
327.85	0.80	-1.1	365.52	14.46	0.6	407.26	164.6	-0.3
329.82	0.95	-0.9	367.74	16.61	-0.3	409.18	180.8	-0.7
331.79	1.12	-1.2	369.53	18.87	0.7	411.21	201.4	-0.1
333.80	1.33	-0.9	371.72	21.59	0.1	413.17	220.6	-0.7
335.78	1.59	0.5	373.53	24.35	0.6	415.17	244.0	-0.4
337.74	1.85	-0.3	375.67	27.68	-0.1	417.11	267.9	-0.4
339.72	2.17	-0.3	377.47	31.28	0.9	419.13	294.8	-0.5
341.76	2.58	0.8	379.65	35.29	-0.4	421.06	324.2	0.0
343.72	2.99	0.2	381.40	39.55	0.4	423.04	355.0	-0.2
345.66	3.48	0.4	383.60	44.51	-0.9	425.00	387.3	-0.5
347.68	4.09	1.2	385.47	50.21	0.1	427.02	428.8	0.5
349.66	4.68	-0.2	387.56	56.45	-0.3	428.95	467.0	0.4
351.63	5.45	0.4	391.51	70.82	-0.2	430.77	511.0	1.3
353.63	6.30	0.3	393.41	77.55	-1.8	432.92	557.4	0.5
355.58	7.31	1.1	395.41	87.62	-0.6	434.90	604.0	0.0
357.59	8.40	0.8	397.36	96.75	-1.4	436.86	660.2	0.5
359.82	9.81	0.7	399.35	108.9	-0.3	438.87	720.4	0.7
361.57	11.12	1.1	401.32	120.2	-0.9	440.85	784.4	0.9
361.59	11.07	0.5	403.30	134.2	-0.3			
363.79	12.85	0.4	406.25	155.8	-0.7			

^aThe estimated uncertainties are ± 0.01 K for the temperatures, $[0.01 + 0.0025(p/\text{Pa})]$ Pa for static pressures below 130 Pa, $[0.1 + 0.0025(p/\text{Pa})]$ Pa for the other static pressures, and ± 0.01 Pa for the effusion pressures. ^b $\Delta p = p - p_{\text{calc}}$. ^cThe reported pressures are the means of the values obtained using the small, medium, and large effusion orifices.

Two Baratron diaphragm capacitance gauges operating at self-controlled temperatures were used for vapor pressure measurements of each compound in both the solid and liquid phases (including supercooled liquid): gauge I, Baratron 631A01TBEH ($T_{\text{gauge}} = 423$ K) for pressures in the range (0.3 to 130) Pa and the sample temperature interval (253 to 413) K; gauge II, Baratron 631A11TBFP ($T_{\text{gauge}} = 473$ K) for pressures in the range (3 to 1330) Pa and the sample temperature interval (253 to 463) K. The results enabled the determination of enthalpies and entropies of sublimation, vaporization, and fusion. The temperatures of the condensed samples were measured using a Pt100 platinum resistance

thermometer (PRT) (class 1/10 DIN in a four-wire connection) that was calibrated by comparison with a standard PRT (25 Ω; Tinsley 5187A). To prevent condensation, the temperature of the tube system between the condensed sample and the pressure gauge was kept at a temperature slightly higher than the temperature of the sample. The uncertainties in the vapor pressure measurements are described by the expressions $\sigma(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$ and $\sigma(p/\text{Pa}) = 0.1 + 0.0025(p/\text{Pa})$ for gauges I and II, respectively. The uncertainty in the temperature measurements was estimated to be ± 0.01 K.

The vapor pressures of the crystalline phases of the two compounds were also measured over the ranges (0.09 and

Table 4. Vapor Pressure Results for 9-Fluoreno^a

<i>T</i>	<i>p</i>		<i>T</i>	<i>p</i>		<i>T</i>	<i>p</i>	
K	Pa	100Δ <i>p</i> / <i>p</i> ^b	K	Pa	100Δ <i>p</i> / <i>p</i> ^b	K	Pa	100Δ <i>p</i> / <i>p</i> ^b
Crystalline Phase (Knudsen Effusion) ^c								
337.16	0.106	2.1	345.09	0.243	−2.7	353.11	0.579	−0.4
339.13	0.132	1.8	347.09	0.307	−0.8	355.10	0.710	−0.3
341.10	0.163	1.0	349.15	0.385	0.0	357.09	0.884	1.5
343.16	0.196	−3.3	351.11	0.470	−0.5	359.09	1.078	1.4
Crystalline Phase (Static)								
350.76	0.51	1.1	374.53	5.04	0.3	400.10	42.77	0.2
352.75	0.62	0.1	376.49	5.99	−0.1	402.11	50.07	0.3
354.71	0.75	−0.8	378.48	7.11	1.1	404.04	57.82	−0.1
356.59	0.92	0.7	380.44	8.55	0.0	406.06	67.38	−0.1
358.67	1.13	0.6	382.39	10.01	−0.3	407.96	77.84	0.0
360.98	1.39	−1.4	384.38	11.83	−0.6	410.00	90.38	−0.2
362.63	1.65	−0.2	386.35	13.93	0.6	411.89	104.0	−0.1
364.58	1.98	−0.7	388.32	16.62	0.3	413.86	121.1	0.8
366.55	2.38	−0.9	390.28	19.50	−1.1	415.85	137.7	−0.7
368.53	2.90	0.3	392.27	22.63	0.2	417.82	159.2	−0.3
370.51	3.43	−1.3	394.22	26.84	0.3	419.78	184.8	0.8
372.48	4.18	0.4	396.22	31.55	0.3	421.73	208.4	−0.8
372.51	4.19	0.4	398.16	36.78	0.3	423.71	241.1	0.1
Liquid Phase								
409.98	118.6	0.0	423.75	253.8	0.0	433.57	423.9	0.8
411.93	133.1	0.4	425.74	282.8	0.4	435.51	460.5	−0.6
413.91	150.0	1.2	427.70	309.6	−0.8	435.52	464.2	0.2
415.88	165.2	−0.2	427.70	313.1	0.3	437.51	509.9	−0.2
417.86	182.2	−1.4	429.67	345.7	0.1	439.47	562.5	0.1
419.81	204.7	−0.3	431.58	381.5	0.3	441.42	615.0	−0.3
421.79	226.6	−0.9	431.60	384.3	0.9			

^aThe estimated uncertainties are ± 0.01 K for the temperatures, $[0.01 + 0.0025(p/\text{Pa})]$ Pa for static pressures below 130 Pa, $[0.1 + 0.0025(p/\text{Pa})]$ Pa for the other static pressures, and ± 0.01 Pa for the effusion pressures. ^b $\Delta p = p - p_{\text{calc}}$. ^cThe reported pressures are the means of the values obtained using the small, medium, and large effusion orifices.

0.98) Pa and (0.11 and 1.08) Pa, respectively, using a Knudsen effusion apparatus enabling the simultaneous operation of nine effusion cells that was described in detail previously.²⁹ The effusion cells were contained in cylindrical holes inside three temperature-controlled aluminum blocks, each of which was kept at a constant temperature different from those of the other two blocks. Each block contained three effusion cells with different effusion orifices: one “small” ($A_o \approx 0.5 \text{ mm}^2$; series A), one “medium” ($A_o \approx 0.8 \text{ mm}^2$; series B), and one “large” ($A_o \approx 1.1 \text{ mm}^2$; series C). Table S1 in the Supporting Information presents the exact orifice areas A_o and Clausing factors w_o of the used effusion orifices, which were made in platinum foil with a thickness of 0.0125 mm. The sample temperatures were assumed to be equal to the temperatures of the respective aluminum blocks, which were measured using Pt100 PRTs (class 1/10 DIN in a four-wire connection). These thermometers were also calibrated by comparison with a standard PRT (25 Ω ; Tinsley 5187 A). The mass loss of the sample due to effusion was determined by weighing the effusion cells to ± 0.01 mg before and after the effusion. At temperature T , the vapor pressure p of the crystalline sample contained in each effusion cell was calculated using eq 1,

$$p = \frac{m}{A_o w_o t} \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (1)$$

where m is the sublimed mass, t is the effusion time period, M is the molar mass of the effusing vapor, and R is the molar gas constant ($8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The uncertainties were

estimated to be better than ± 0.01 Pa and ± 0.01 K, respectively, for the pressure and temperature measurements.

Computational Details. Standard ab initio molecular orbital calculations³⁰ were performed with the Gaussian 09 suite of programs.³¹ The energies of the compounds studied were calculated using two different theoretical model chemistry Gaussian- n (Gn) methods, namely, G3³² and G4.³³ Details of these methods were given in our previous paper on fluoranthene.¹⁰ Energies at 0 K and enthalpies at 298 K for 9-fluoreno¹⁰, 9-fluorenone, and a reference set of 26 oxygen-containing cyclic hydrocarbons are collected in Table S2 in the Supporting Information.

RESULTS AND DISCUSSION

Combustion Calorimetry Results. The combustion reactions of 9-fluorenone, $\text{C}_{13}\text{H}_8\text{O}$, and 9-fluoreno¹⁰, $\text{C}_{13}\text{H}_{10}\text{O}$, are described by eqs 2 and 3, respectively:



The internal energy for the isothermal bomb process, $\Delta U(\text{IBP})$, for each compound was calculated using eq 4:

$$\Delta U(\text{IBP}) = -[\epsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \epsilon_f] \Delta T_{\text{ad}} + \Delta U(\text{ign}) \quad (4)$$

Table 5. Thermodynamic Parameters Derived from the Fits of the Clarke and Glew Equation to the Measured Vapor Pressures ($p^\circ = 0.1$ MPa)

phase	T/K range	θ K	$\Delta_{\text{cd}}^{\text{g}}G_{\text{m}}^\circ(\theta)$ kJ·mol ⁻¹	$p(\theta)$ Pa	$\Delta_{\text{cd}}^{\text{g}}H_{\text{m}}^\circ(\theta)$ kJ·mol ⁻¹	$\Delta_{\text{cd}}^{\text{g}}S_{\text{m}}^\circ(\theta)$ J·K ⁻¹ ·mol ⁻¹	R^2	$-\Delta_{\text{cd}}^{\text{g}}C_{p,\text{m}}^\circ(\theta)$ J·K ⁻¹ ·mol ⁻¹	100·s ^a
9-Fluorenone									
crystalline	326.9 to 352.1	298.15	38.82 ± 0.03	1.6·10 ⁻²	95.1 ± 0.5 ^b	188.8 ± 0.7	0.9999	31.5 ± 10.5 ^c	0.8
		339.51 ^d	31.10 ± 0.01	1.6	93.8 ± 0.2				
		354.59 ^e	28.32 ± 0.01	6.7	93.4 ± 0.3				
liquid ^g	312.2 to 334.1 327.8 to 440.8	298.15 ^f	38.75 ± 0.03	1.6·10 ⁻²	94.7 ± 0.4	187.7 ± 1.0	0.9999		0.9
		298.15	36.25 ± 0.02	4.5·10 ⁻²	80.6 ± 0.2	148.8 ± 0.7	1.0000	94.1 ± 2.3 ^h	0.7
		384.35 ^d	24.49 ± 0.01	47	72.5 ± 0.1				
		354.59 ^e	28.32 ± 0.01	6.7	75.3 ± 0.1				
9-Fluorenol									
crystalline	350.8 to 423.7	298.15	46.32 ± 0.06	7.7·10 ⁻⁴	108.3 ± 0.5 ^b	207.9 ± 1.7	1.0000	44.3 ± 6.1 ^h	0.6
		387.24 ^d	28.33 ± 0.01	15	104.4 ± 0.1				
		426.83 ^e	20.64 ± 0.01	3.0·10 ²	102.6 ± 0.1				
liquid ^g	337.2 to 359.1 410.0 to 441.4	298.15 ^f	46.67 ± 0.11	6.7·10 ⁻⁴	109.0 ± 0.8	209.0 ± 2.7	0.9995		1.8
		298.15	40.32 ± 0.07	8.6·10 ⁻³	91.6 ± 0.4	172.0 ± 0.7	0.9998	99.1 ± 2.3 ^c	0.6
		425.70 ^d	20.79 ± 0.01	2.8·10 ²	78.9 ± 0.2				
		426.83 ^e	20.64 ± 0.01	3.0·10 ²	78.8 ± 0.2				

^as is the standard deviation of the fit, defined as $s = [\sum_{i=1}^n (\ln p - \ln p_{\text{calc}})^2 / (n - m)]^{1/2}$, where n is the number of experimental points used in the fit and m is the number of adjustable parameters in the Clarke and Glew equation. ^bSelected result. ^cEstimated value. ^dMean temperature. ^eTemperature of the triple point. ^fKnudsen effusion. ^gIncluding supercooled liquid. ^hAdjustable parameter.

In this equation, ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange and the work of stirring and $\Delta m(\text{H}_2\text{O})$ is the difference between the mass of water added to the calorimeter and 2900.0 g; the remaining terms were previously defined in the literature.³⁴

The detailed results of the individual combustion experiments for 9-fluorenone and 9-fluorenol are presented in Tables S3 and S4 in the Supporting Information, respectively (no soot or carbon residue was observed in any of the experiments). The mean values of the standard massic energy of combustion, $\langle \Delta_c u^\circ \rangle$, are presented in Table 2. The derived standard molar values for the combustion energy, $\Delta_c U_{\text{m}}^\circ(\text{cr})$, and enthalpy, $\Delta_c H_{\text{m}}^\circ(\text{cr})$, as well as the values of the standard molar enthalpy of formation in the crystalline phase, $\Delta_f H_{\text{m}}^\circ(\text{cr})$, at $T = 298.15$ K are also given in this table. To derive $\Delta_f H_{\text{m}}^\circ(\text{cr})$ from $\Delta_c H_{\text{m}}^\circ$, the standard molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ·mol⁻¹ and $-(393.51 \pm 0.13)$ kJ·mol⁻¹,³⁵ respectively, were used. The derived result for 9-fluorenone, $\Delta_f H_{\text{m}}^\circ(\text{cr}) = -(11.4 \pm 3.8)$ kJ·mol⁻¹, lies between the two existing literature values for this property and is in agreement with the value derived by Verevkin⁷ within the experimental uncertainty.

Vapor Pressures and Phase Transitions. The vapor pressure results measured for condensed phases of 9-fluorenone and 9-fluorenol are presented in Tables 3 and 4, respectively. These tables include vapor pressures measured using two different methods: a static method (diaphragm capacitance gauge) and the mass-loss Knudsen effusion method. The values of the effusion vapor pressures presented in these tables are the means of the results derived from the individual effusion cells at each temperature. The experimental results obtained from each effusion cell, which are presented in detail in the Supporting Information (Table S5 for 9-fluorenone and Table S6 for 9-fluorenol), show that the measured pressure was not significantly dependent on the size of the effusion orifice. The truncated form of the Clarke and Glew equation (eq 5)³⁶ was used to fit the results of crystalline and liquid vapor pressures:

$$R \ln \left(\frac{p}{p^\circ} \right) = -\frac{\Delta_{\text{cd}}^{\text{g}}G_{\text{m}}^\circ(\theta)}{\theta} + \Delta_{\text{cd}}^{\text{g}}H_{\text{m}}^\circ(\theta) \left(\frac{1}{\theta} - \frac{1}{T} \right) + \Delta_{\text{cd}}^{\text{g}}C_{p,\text{m}}^\circ(\theta) \left[\left(\frac{\theta}{T} \right) - 1 + \ln \left(\frac{T}{\theta} \right) \right] \quad (5)$$

In this equation, p is the vapor pressure at temperature T , p° is a selected reference pressure ($p^\circ = 0.1$ MPa in this work), θ is a selected reference temperature, R is the molar gas constant, and $\Delta_{\text{cd}}^{\text{g}}G_{\text{m}}^\circ(\theta)$, $\Delta_{\text{cd}}^{\text{g}}H_{\text{m}}^\circ(\theta)$, and $\Delta_{\text{cd}}^{\text{g}}C_{p,\text{m}}^\circ(\theta)$ represent the differences in the molar Gibbs energies, molar enthalpies, and molar constant-pressure heat capacities of the gaseous and condensed phases, respectively, at the reference temperature θ . The results for $\Delta_{\text{cd}}^{\text{g}}H_{\text{m}}^\circ(\theta)$, $\Delta_{\text{cd}}^{\text{g}}G_{\text{m}}^\circ(\theta)$, and $\Delta_{\text{cd}}^{\text{g}}C_{p,\text{m}}^\circ(\theta)$ derived from the fits to eq 5 are presented in Table 5. The values of $\Delta_{\text{cd}}^{\text{g}}S_{\text{m}}^\circ(\theta)$ were calculated as $\{[\Delta_{\text{cd}}^{\text{g}}H_{\text{m}}^\circ(\theta) - \Delta_{\text{cd}}^{\text{g}}G_{p,\text{m}}^\circ(\theta)]/\theta\}$, and the values of $p(\theta)$ were determined using the equation $[\Delta_{\text{cd}}^{\text{g}}G_{\text{m}}^\circ(\theta) = -R\theta \ln(p/p^\circ)]$. From our own experience, when accurate experimental crystalline or liquid vapor pressures measured over more than ca. 50 K are available, the fit of eq 5 to the experimental data may yield reliable values of $\Delta_{\text{cd}}^{\text{g}}C_{p,\text{m}}^\circ(\theta)$. For 9-fluorenone, the value $\Delta_f^{\text{f}}C_{p,\text{m}}^\circ(298.15 \text{ K}) = -(94.1 \pm 2.3)$ J·K⁻¹·mol⁻¹ was derived from the least-squares regression of the fit of eq 5 to the liquid vapor pressure–temperature data over a very large temperature range (113 K). For 9-fluorenol, however, liquid vapor pressures were measured over a temperature interval of 31.9 K, and the fit did not yield a reliable value of $\Delta_f^{\text{f}}C_{p,\text{m}}^\circ(298.15 \text{ K})$. The value $\Delta_f^{\text{f}}C_{p,\text{m}}^\circ(298.15 \text{ K}) = -(99.1 \pm 2.3)$ J·K⁻¹·mol⁻¹ was estimated for this compound from the value of $\Delta_f^{\text{f}}C_{p,\text{m}}^\circ(298.15 \text{ K})$ derived for 9-fluorenone by considering the replacement of C=O for C–OH according to the group contribution values proposed by Chickos et al.³⁷ The value $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^\circ(298.15 \text{ K}) = -(44.3 \pm 6.1)$ J·K⁻¹·mol⁻¹ was derived for 9-fluorenol from the least-squares regression of the fit of eq 5 to the solid vapor pressure–temperature data measured over a temperature interval of 73 K. For 9-fluorenone, the fit did not yield a reliable value of $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^\circ(298.15 \text{ K})$ because of the narrow temperature range of

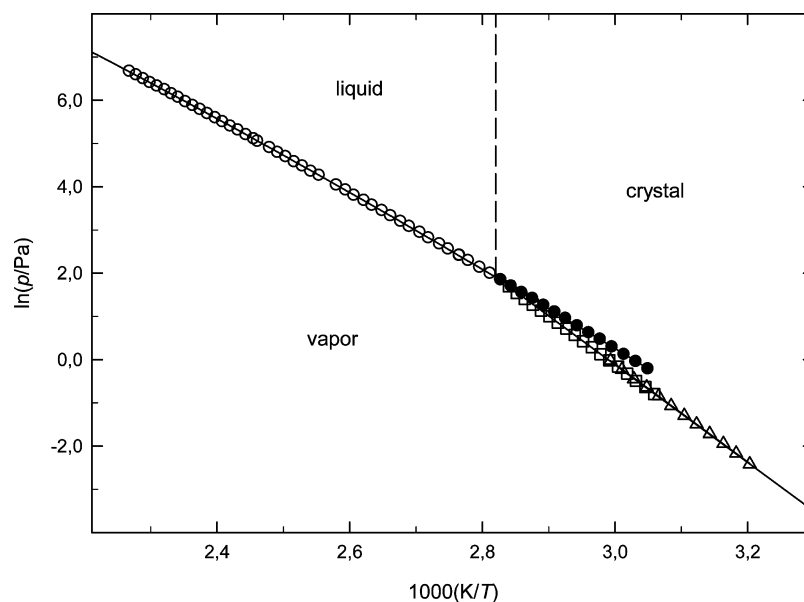


Figure 2. Phase diagram of 9-fluorenone: ○, static liquid vapor pressures; ●, undercooled liquid vapor pressures; □, static crystalline vapor pressures; △, effusion vapor pressures (means of results for the small, medium, and large orifices). Triple point coordinates: $T = 354.59$ K, $p = 6.73$ Pa.

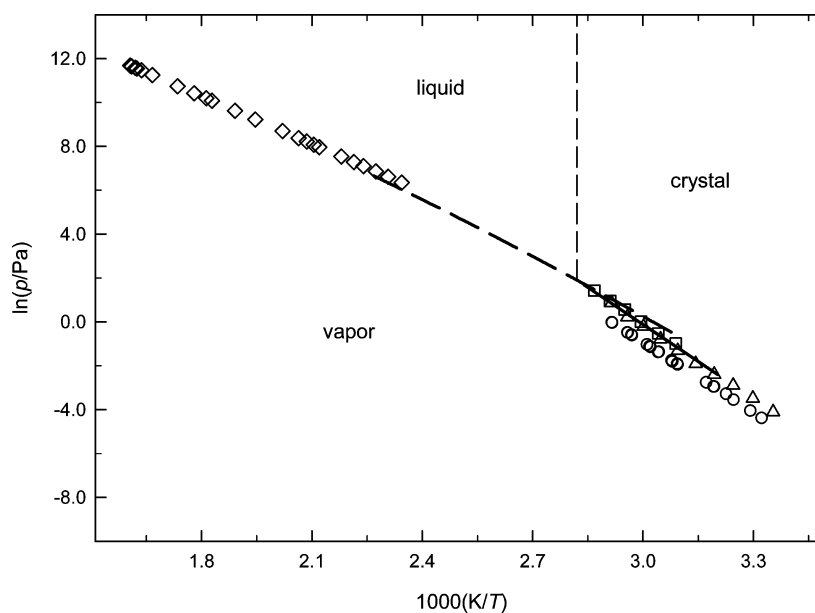


Figure 3. Comparison of literature vapor pressure results for 9-fluorenone and with the ones obtained in this work. Solid line, smoothed vapor pressure results for the crystalline phase derived in this work; dashed line, smoothed vapor pressure results for the liquid phase derived in this work; □, crystalline-phase vapor pressure results from ref 7; △, crystalline-phase vapor pressure results from ref 8; ○, crystalline-phase vapor pressure results from ref 9; ◇, liquid-phase vapor pressure results from ref 12.

the measured solid pressures (25.2 K). For this compound, the value $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ}(298.15 \text{ K}) = -(31.5 \pm 10.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was estimated using eq 6 proposed by Monte et al.,³⁸

$$\frac{\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ}(298.15 \text{ K})}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = - \left\{ 0.9 + 0.176 \left[\frac{C_{p,m}^{\circ}(\text{g})}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right] \right\} \quad (6)$$

using the value $C_{p,m}^{\circ}(\text{g}) = 173.98 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ calculated in this work at the B3LYP/6-31G(2df,p) level of theory and assigning an (arbitrary) uncertainty of one-third of the estimated value.

Equation 6 was derived from eq 7, which was published by Chickos et al.:³⁹

$$\frac{\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ}(298.15 \text{ K})}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = - \left\{ 0.75 + 0.15 \left[\frac{C_{p,m}^{\circ}(\text{cr})}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right] \right\} \quad (7)$$

The vapor pressures and enthalpies of sublimation at 298.15 K derived from the two different experimental methods (Knudsen effusion and static) for the two compounds are in good agreement despite the different ranges of the (p , T) measurements. Figure 2 presents the pressure–temperature

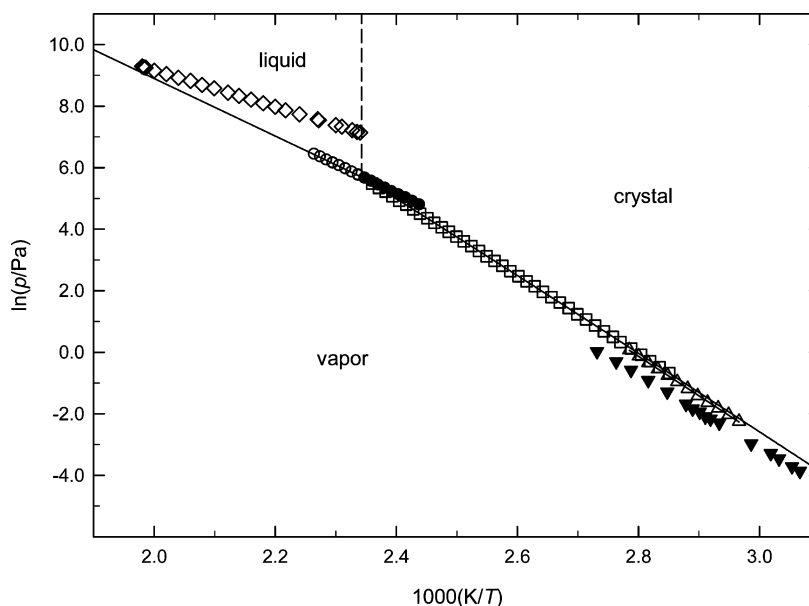


Figure 4. Phase diagram of 9-fluorenol: ○, static liquid vapor pressures; ●, undercooled liquid vapor pressures; □, static crystalline vapor pressures; △, effusion vapor pressures (means of results for the small, medium, and large orifices). Triple point coordinates: $T = 426.83$ K, $p = 297.9$ Pa. Literature data: ▼, crystalline-phase vapor pressure results from ref 9; ◇, liquid-phase vapor pressure results from ref 12.

phase diagrams for 9-fluorenone, while in Figure 3 literature results for the vapor pressure of 9-fluorenone are compared with the ones obtained in the present work. Results previously reported in the literature for both 9-fluorenone and 9-fluorenol were recalculated in the present work using the heat capacity differences presented in Table 5. There is excellent agreement between the results calculated from the data presented by Sivaraman et al.¹² for liquid 9-fluorenone [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = 80.7 \text{ kJ}\cdot\text{mol}^{-1}$, $p(T = 298.15 \text{ K}) = 5.3\cdot 10^{-2} \text{ Pa}$] and our values presented in Table 5. For the sublimation of 9-fluorenone, the results calculated from the data previously reported by Hansen and Eckert⁸ [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (93.0 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$, $p(T = 298.15 \text{ K}) = 1.6\cdot 10^{-2} \text{ Pa}$] and by Verevkin⁷ [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (92.9 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$, $p(T = 298.15 \text{ K}) = 1.9\cdot 10^{-2} \text{ Pa}$] are also in good agreement with our results, although our value for the enthalpy of sublimation is ca. $2 \text{ kJ}\cdot\text{mol}^{-1}$ higher. The results calculated from the data recently published by Goldfarb and Suuberg⁹ [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (89.2 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$, $p(T = 298.15 \text{ K}) = 9.0\cdot 10^{-3} \text{ Pa}$], reveal lower values of the measured vapor pressures and an enthalpy of sublimation $6 \text{ kJ}\cdot\text{mol}^{-1}$ lower than the result derived in the present work. The difference between the enthalpy of sublimation of 9-fluorenone and that of fluorene [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (87.8 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$]² is $7.3 \text{ kJ}\cdot\text{mol}^{-1}$, a value equal to the difference between the enthalpies of sublimation of anthrone [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (107.6 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$]⁴⁰ and anthracene [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (100.2 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$].²⁹ The enthalpy of sublimation of 9-fluorenone was also determined calorimetrically using the Calvet drop technique.²⁵ The value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(367.7 \text{ K}) = (105.8 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ derived from five independent experiments was converted to $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (92.2 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ using the difference [$H_{\text{m}}^{\circ}(\text{g}, 367.7 \text{ K}) - H_{\text{m}}^{\circ}(\text{g}, 298.15 \text{ K})$] = $13.6 \text{ kJ}\cdot\text{mol}^{-1}$, which was calculated by taking into account the theoretically calculated values of the gas-phase heat capacity, at constant volume, between 290 and 500 K (Table S7 in the Supporting Information). The values of gas-phase heat capacity, at constant pressure, calculated as $C_{p,\text{m}}^{\circ}(\text{g}) = C_{v,\text{m}}^{\circ}(\text{g}) + R$ (where R is the molar gas constant), are

well-fitted by the second-degree polynomial $C_{p,\text{m}}^{\circ}(\text{g})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -52.15 + 0.894(T/\text{K}) - 4.55\cdot 10^{-4}(T/\text{K})^2$. The calorimetric result $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (88.4 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ determined by Sabbah et al.⁶ is $3.8 \text{ kJ}\cdot\text{mol}^{-1}$ lower than our calorimetric value.

Figure 4 presents the vapor pressures of 9-fluorenol determined in the present work and the ones available in the literature. From the data published by Sivaraman et al.¹² for liquid 9-fluorenol, we derived the results $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = 65.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $p(T = 298.15 \text{ K}) = 7.9\cdot 10^{-1} \text{ Pa}$, which are in large disagreement with our results. On the other hand, from the data published by Goldfarb and Suuberg⁹ for sublimation of 9-fluorenol, we calculated the results $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (99.5 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ and $p(T = 298.15 \text{ K}) = 6.7\cdot 10^{-4} \text{ Pa}$. Although the extrapolated vapor pressure at 298.15 K is close to our result, the measurements performed by those researchers at higher temperatures are clearly lower than ours, as shown in Figure 4, yielding an enthalpy of sublimation that is ca. $9 \text{ kJ}\cdot\text{mol}^{-1}$ lower than the value derived in the present work. Comparing the sublimation results for fluorene² with the results presently derived for 9-fluorenol, we conclude that the enthalpy of sublimation of 9-fluorenol is ca. $20 \text{ kJ}\cdot\text{mol}^{-1}$ higher than that of fluorene. This difference is similar to the observed difference between the enthalpy of sublimation of phenol [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (69.7 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$]⁴¹ and that of benzene, which was calculated in this work as $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (48.5 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$ using the published vapor pressures⁴² and the value $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\circ} = -(27 \pm 3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$;⁴² it is also similar to the difference between the enthalpy of sublimation of 1-naphthol determined by Colomina and Roux [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(304.5 \text{ K}) = (91.2 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$]⁴³ and the enthalpy of sublimation of naphthalene, determined by Monte et al. [$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (72.70 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$].²⁸

The values of the temperatures and enthalpies of fusion determined directly from the DSC experiments and indirectly from the enthalpies of sublimation and vaporization derived from the static vapor pressure measurements are listed in Table 6. The DSC thermograms did not show any crystalline

Table 6. Temperatures and Molar Enthalpies of Fusion of the Studied Compounds

compound	T_{tp} K	T_{fus} K	$\Delta_{\text{cr}}^{\text{f}}H_{\text{m}}^{\circ}(T^{\text{a}})$ kJ·mol ⁻¹	$\Delta_{\text{cr}}^{\text{f}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ kJ·mol ⁻¹	method	ref
9-fluorenone	354.59	356.16 ± 0.22	17.6 ± 0.7	14.5 ± 0.2	DSC	this work
			18.1 ± 0.2		static vp	this work
		356.4	18.12		calorimetric	44
		353.3			calorimetric	7
9-fluorenol	426.83	428.70 ± 0.07	24.2 ± 0.7	16.7 ± 0.5	DSC	this work
			23.8 ± 0.2		static vp	this work

^a T_{fus} (calorimetric) or T_{tp} (static vapor pressure measurements).

Table 7. Standard ($p^{\circ} = 0.1 \text{ MPa}$) Molar Absolute Entropies of Fluorene, 9-Fluorenol, and 9-Fluorenone and Standard Molar Enthalpies, Entropies, and Gibbs Energies of Oxidation Reactions at $T = 298.15 \text{ K}$

	$S_{\text{m}}^{\circ}(\text{g})^{\text{a}}$ J·K ⁻¹ ·mol ⁻¹	$S_{\text{m}}^{\circ}(\text{cr})$ J·K ⁻¹ ·mol ⁻¹	$\Delta_{\text{oxid}}H_{\text{m}}^{\circ}$ kJ·mol ⁻¹	$\Delta_{\text{oxid}}S_{\text{m}}^{\circ}$ J·K ⁻¹ ·mol ⁻¹	$\Delta_{\text{oxid}}G_{\text{m}}^{\circ}$ kJ·mol ⁻¹
fluorene	381.0	203.7 ± 0.5	-157.9 ± 4.2 ^b -388.8 ± 4.8 ^c	-118.8 ± 1.8 ^b -115.5 ± 0.9 ^c	-122.5 ± 4.2 ^b -354.4 ± 4.8 ^c
fluorenol	395.4	187.5 ± 1.7	-230.9 ± 4.8 ^d	3.3 ± 1.8 ^d	-231.9 ± 4.8 ^d
fluorenone	412.2	223.4 ± 0.7			

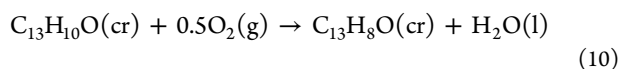
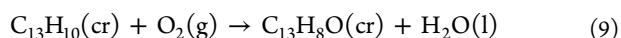
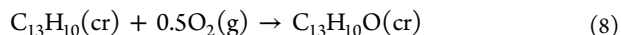
^aTheoretical values calculated at the B3LYP/6-31G(2df,p) level and corrected by applying the scale factor 0.9946 in S_{vib} (taken from ref 45).

^bEquation 8. ^cEquation 9. ^dEquation 10.

transitions between 298 K and the temperature of fusion of each compound. For 9-fluorenone, the value of the triple-point temperature, T_{tp} , obtained from the intersection of the static liquid-phase and solid-phase vapor pressure equations is 1.6 K lower than the value determined in this work by the DSC technique, 1.8 K lower than the one published by Acree,⁴⁴ and 1.3 K higher than the calorimetric result presented by Verevkin.⁷ The calorimetric enthalpy of fusion of this compound is also close to the value derived indirectly from the sublimation and vaporization enthalpies and to the literature results.^{7,44}

For 9-fluorenol, T_{tp} is 1.9 K lower than the value of T_{fus} derived from the calorimetric experiments, and the enthalpies of fusion derived from these different techniques are equal within the experimental uncertainty. The closeness of the temperatures and enthalpies of fusion determined from the calorimetric technique and those derived indirectly from the vaporization and sublimation curves confers additional reliability to the results derived in this study and led us to select the enthalpies of sublimation derived from the static vapor pressure measurements for both compounds studied.

Oxidation of Fluorene to 9-Fluorenol and 9-Fluorenone. The oxidations of fluorene, $\text{C}_{13}\text{H}_{10}$, to 9-fluorenol, $\text{C}_{13}\text{H}_{10}\text{O}$, and to 9-fluorenone, $\text{C}_{13}\text{H}_8\text{O}$, are described by eqs 8 and 9, respectively, while the oxidation of 9-fluorenol to 9-fluorenone is represented by eq 10.



To establish quantitatively the thermodynamic tendencies for the oxidations of fluorene and 9-fluorenol, we calculated the values of $\Delta_{\text{oxid}}G_{\text{m}}^{\circ}$ presented in Table 7 using the well-known relation $\Delta_{\text{r}}G_{\text{m}}^{\circ}(\theta) = \Delta_{\text{r}}H_{\text{m}}^{\circ}(\theta) - \theta\Delta_{\text{r}}S_{\text{m}}^{\circ}$. The values of $\Delta_{\text{oxid}}H_{\text{m}}^{\circ}$ were calculated from the enthalpies of formation of fluorene [$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K}) = (91.6 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$]² and those of 9-

fluorenol and 9-fluorenone presented in Table 2. For water, the value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{l}, 298.15 \text{ K}) = -(285.830 \pm 0.042) \text{ kJ}\cdot\text{mol}^{-1}$ was used.³⁵ The values of $\Delta_{\text{oxid}}S_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K})$ were calculated from the values of $S_{\text{m}}^{\circ}(\text{g})$ presented in Table 7, which were determined by calculations at the B3LYP/6-31G(2df,p) level, and the values of $\Delta_{\text{cr}}^{\text{f}}S_{\text{m}}^{\circ}(298.15 \text{ K})$ presented in Table 5, which were derived from the static vapor pressures of 9-fluorenol and 9-fluorenone. For fluorene, the literature value $\Delta_{\text{cr}}^{\text{f}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (177.3 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was used.² The entropies of oxygen and liquid water were taken as $S_{\text{m}}^{\circ}(\text{g}, 298.15 \text{ K}) = 205.15 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $S_{\text{m}}^{\circ}(\text{l}, 298.15 \text{ K}) = 69.95 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.⁴⁶

Experimental and Theoretical Enthalpies of Formation in the Gas Phase. Table 8 lists the derived standard molar enthalpies of formation in the gas phase, $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})$, at $T = 298.15 \text{ K}$ derived from the experimental results for the compounds studied in this work. The standard procedure for

Table 8. Gas-Phase Enthalpies of Formation, $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})$, at $T = 298.15 \text{ K}$ for the Compounds Studied, Calculated Using the Quantum-Chemical Methods G3 and G4 and from Experimental Measurements (All Values in $\text{kJ}\cdot\text{mol}^{-1}$)

method	9-fluorenone	9-fluorenol
experimental	83.7 ± 3.8 ^a	42.0 ± 2.9 ^a
atomization, G3	80.3 (81.8 ^b)	29.9 (31.8 ^b)
atomization, G4	78.2 (80.4 ^c)	26.9 (29.1 ^c)
bond separation (eqs 13 and 14), G3	74.5	21.3
bond separation (eqs 13 and 14), G4	76.0	20.8
isodesmic (eqs 15 and 17), G3	79.0	23.8
isodesmic (eqs 15 and 17), G4	80.5	23.9
isodesmic (eqs 16 and 18), G3	78.8	30.6
isodesmic (eqs 16 and 18), G4	80.8	30.6

^aValues determined from the enthalpies of formation in the crystalline phase (Table 2) and the enthalpies of sublimation derived from the static vapor pressure measurements (Table 5). ^bValue corrected using eq 11. ^cValue corrected using eq 12.

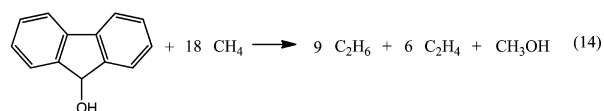
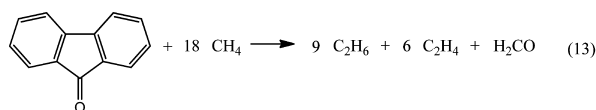
obtaining enthalpies of formation in *Gn* theories is to use atomization reactions.^{47,48} The enthalpies of formation for 9-fluorenone and 9-fluorenol calculated at the G3 and G4 levels of theory are collected in Table 8. We calibrated the theoretical methods used in this work to obtain more reliable enthalpies of formation by comparing the calculated and experimental enthalpies of formation for a series of oxygen-containing cyclic hydrocarbons with known values available in the literature. We used a set of 26 compounds ranging from cyclopentanol and cyclopentanone to dibenzofuran and anthraquinone. The calculated enthalpies of formation for these compounds at the G3 and G4 levels as well as the corresponding experimental values are collected in Table S8 in the Supporting Information. As shown in Table S8, the G3 and G4 calculations gave good results, with mean absolute deviations of 4.3 kJ·mol⁻¹ (G3) and 3.2 kJ·mol⁻¹ (G4). Very good linear correlations between the experimental and calculated enthalpies of formation were obtained for the set of compounds of Table S8:

$$\frac{\Delta_f H_m^\circ(\text{exptl})}{\text{kJ}\cdot\text{mol}^{-1}} = (0.9916 \pm 0.0038) \left[\frac{\Delta_f H_m^\circ(\text{G3})}{\text{kJ}\cdot\text{mol}^{-1}} \right] + (2.15 \pm 1.02) \quad (11)$$

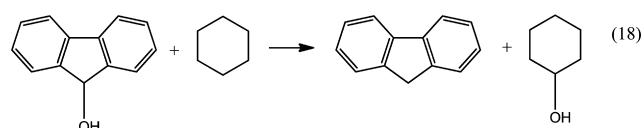
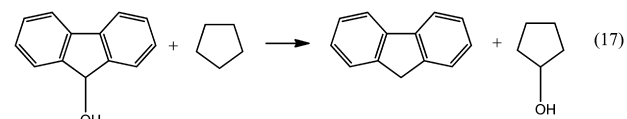
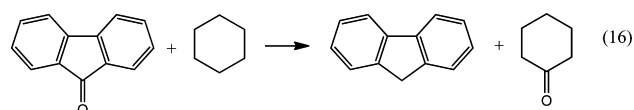
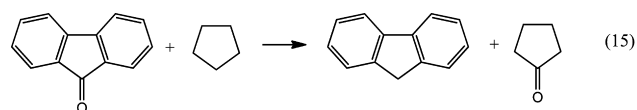
for G3 ($n = 26$, $R = 0.99982$, standard deviation = 3.2 kJ·mol⁻¹) and

$$\frac{\Delta_f H_m^\circ(\text{exptl})}{\text{kJ}\cdot\text{mol}^{-1}} = (0.9999 \pm 0.0037) \left[\frac{\Delta_f H_m^\circ(\text{G4})}{\text{kJ}\cdot\text{mol}^{-1}} \right] + (2.25 \pm 0.97) \quad (12)$$

for G4 ($n = 26$, $R = 0.99984$, standard deviation = 3.1 kJ·mol⁻¹). The calculated enthalpies of formation for 9-fluorenol and 9-fluorenone were corrected using eqs 11 and 12, and the values are collected in Table 8. The agreement between the experimental and calculated values is very good in the case of 9-fluorenone, with deviations of (2 to 3) kJ·mol⁻¹, confirming the reliability of our measurements. For 9-fluorenol the deviations are higher, (10 to 13) kJ·mol⁻¹. Glukhovtsev and Laiter⁴⁹ showed that more accurate heats of formation can be derived using isodesmic or homodesmotic reactions⁵⁰ rather than atomization energies. Following Raghavachari et al.,⁵¹ we used "bond-separation isodesmic reactions",³⁰ in which all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages, to derive the theoretical enthalpies of formation. The bond separation reactions for 9-fluorenone and 9-fluorenol are given by eqs 13 and 14, respectively. We also used the set of

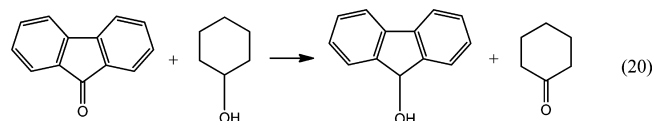
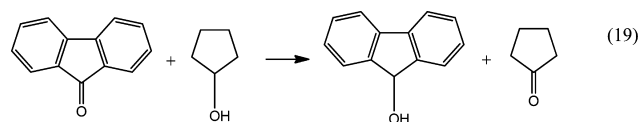


isodesmic reactions given by eqs 15 to 18 to calculate the enthalpies of formation of 9-fluorenone and 9-fluorenol. The values of the enthalpies of formation of 9-fluorenone and 9-fluorenol calculated using the bond-separation isodesmic



reactions 13 and 14 and the isodesmic reactions 15 to 18 are collected in Table 8 (the experimental values used for the reference molecules are collected in Table S9 in the Supporting Information). Again, the agreement between the experimental and calculated values is better for 9-fluorenone than for 9-fluorenol. The worst results are those obtained using bond-separation isodesmic reactions, probably because this type of reaction does not allow the correct balance between reagents and products when some characteristics, such as aromaticity, are present on only one side of the reaction as a result of the bond breaking process.

We can also apply another set of two isodesmic reactions (eqs 19 and 20) that use the pairs cyclopentanol/cyclo-



pentanone and cyclohexanol/cyclohexanone as references in order to calculate the difference between the enthalpies of formation of the two compounds. Finally, we can calculate the difference between the enthalpies of formation of 9-fluorenone and 9-fluorenol using the hydrogenation reaction. The results are shown in Table 9. The values calculated using isodesmic reaction 20 and hydrogenation reaction 21 are in reasonable agreement with the experimental value measured in this work.

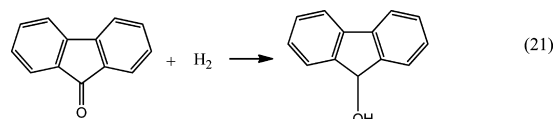


Table 9. Experimental and Calculated Differences between the Enthalpies of Formation of 9-Fluorenone and 9-Fluorenol (All Values in $\text{kJ}\cdot\text{mol}^{-1}$)

method	$\Delta_f H_m^\circ(\text{g})$ difference
	$\text{kJ}\cdot\text{mol}^{-1}$
experimental	41.7 ± 4.8
isodesmic (eq 19), G3	55.2
isodesmic (eq 19), G4	56.6
isodesmic (eq 20), G3	48.3
isodesmic (eq 20), G4	50.2
hydrogenation (eq 21), G3	48.5
hydrogenation (eq 21), G4	49.9

We can compare the energetics of reactions 19 and 20 calculated using the experimental and computational enthalpies of formation of 9-fluorenone and 9-fluorenol obtained in this work with that obtained from the Gibbs energies directly derived from the experimental solution-phase redox potentials measured in 1949 by Adkins et al.⁵² If it is assumed that the solution phase effects cancel, the $\Delta_r G$ values are $1.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $8.8 \text{ kJ}\cdot\text{mol}^{-1}$ for reactions 19 and 20, respectively. Using the values taken from G3 calculations for the entropies of the compounds included in both reactions, we calculated $\Delta_r G$ values of $3.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $6.6 \text{ kJ}\cdot\text{mol}^{-1}$ for reactions 19 and 20, respectively. When the experimental values obtained in this work were used, the calculated $\Delta_r G$ values for reactions 19 and 20 were $11.4 \text{ kJ}\cdot\text{mol}^{-1}$ and $14.9 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

■ ASSOCIATED CONTENT

● Supporting Information

Tables S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mjmonte@fc.up.pt.

Funding

Thanks are due to Fundação para a Ciência e Tecnologia (FCT) (Lisbon, Portugal) and FEDER for financial support to Centro de Investigação em Química - UP and financing for the research project PTDC/QUI-QUI/102814/2008. R.N. thanks the Spanish Ministerio de Ciencia e Innovación for financial support under Project CTQ2010-16402. A.R.R.P.A. and A.I.M.C.L.F. thank FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the awards of a Ph.D. research grant (SFRH/BD/39210/2007) and a postdoctoral fellowship (SFRH/BPD/27053/2006), respectively. L.M.P.F.A. thanks Programa Ciência 2008 (PEst-C/QUI/UI0081/2011).

Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Zhang, X.; Ji, X.; Jiang, S.; Liu, L.; Weeks, B. L.; Zhang, Z. Highly efficient synthesis of 9-fluorenone from 9H-fluorenes by air oxidation. *Green Chem.* **2011**, *13*, 1891–1896.
- (2) Monte, M. J. S.; Pinto, S. P.; Lobo Ferreira, A. I. M. C.; Amaral, L. M. P. F.; Freitas, V. L. S.; Ribeiro da Silva, M. D. M. C. Fluorene: An extended experimental thermodynamic study. *J. Chem. Thermodyn.* **2012**, *45*, 53–58.
- (3) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. Donor–acceptor

9-uncapped fluorenes and fluorenone as stable blue light emitters. *Org. Lett.* **2009**, *11*, 1289–1292.

(4) Forrest, S. R. Ultrathin organic films grown by organic molecular beam deposition and related techniques. *Chem. Rev.* **1997**, *97*, 1793–1896.

(5) Forrest, S. R. The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* **2004**, *428*, 911–918.

(6) Sabbah, R.; El Watik, L.; Minadakis, C. Thermodynamic study of 9-fluorenone. *C. R. Acad. Sci. Paris* **1988**, *307*, 239–244.

(7) Verevkin, S. P. Thermochemistry of Aromatic Ketones. Experimental Enthalpies of Formation and Structural Effects. *Thermochim. Acta* **1998**, *310*, 229–235.

(8) Hansen, P. C.; Eckert, C. A. An Improved Transpiration Method for the Measurement of Very Low Vapor Pressures. *J. Chem. Eng. Data* **1986**, *31*, 1–3.

(9) Goldfarb, J. L.; Suuberg, E. M. Vapor Pressures and Sublimation Enthalpies of Seven Heteroatomic Aromatic Compounds Measured via the Knudsen Effusion Technique. *J. Chem. Thermodyn.* **2010**, *42*, 781–786.

(10) Monte, M. J. S.; Notario, R.; Pinto, S. P.; Lobo Ferreira, A. I. M. C.; Ribeiro da Silva, M. D. M. C. Thermodynamic Properties of Fluoranthene: An Experimental and Computational Study. *J. Chem. Thermodyn.* **2012**, *49*, 159–164.

(11) Luss, H. R.; Smith, D. L. The Crystal and Molecular Structure of 9-Fluorenone. *Acta Crystallogr.* **1972**, *B28*, 884–887.

(12) Sivaraman, A.; Martin, R. J.; Kobayashi, R. A Versatile Apparatus To Study the Vapor Pressures and Heats of Vaporization of Carbazole, 9-Fluorenone and 9-Hydroxyfluorene at Elevated Temperatures. *Fluid Phase Equilib.* **1983**, *12*, 175–188.

(13) Wieser, M. E.; Berglund, M. Atomic weights of the elements 2009 (IUPAC Technical Report). *Pure Appl. Chem.* **2011**, *83*, 359–396.

(14) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Planas Leitão, M. L.; Roux, M. V.; Torres, L. A. Reference materials for calorimetry and differential thermal analysis. *Thermochim. Acta* **1999**, *331*, 93–204.

(15) Gundry, H. A.; Harrop, D.; Head, A. J.; Lewis, G. B. Thermodynamic properties of organic oxygen compounds 21. Enthalpies of combustion of benzoic acid, pentan-1-ol, octan-1-ol, and hexadecan-1-ol. *J. Chem. Thermodyn.* **1969**, *1*, 321–332.

(16) Bickerton, J.; Pilcher, G.; Al-Takhin, G. Enthalpies of combustion of the three aminopyridines and the three cyanopyridines. *J. Chem. Thermodyn.* **1984**, *16*, 373–378.

(17) Ribeiro da Silva, M. D. M. C.; Santos, L. M. N. B. F.; Silva, A. L. R. O.; Fernandes, Ó.; Acree, W. E., Jr. Energetics of 6-methoxyquinoline and 6-methoxyquinoline N-oxide: The dissociation enthalpy of the (N–O) bond. *J. Chem. Thermodyn.* **2003**, *35*, 1093–1100.

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

(19) Santos, L. M. N. B. F. Ph.D. Thesis, University of Porto, Porto, Portugal, 1995.

(20) Santos, L. M. N. B. F.; Silva, M. T.; Schröder, B.; Gomes, L. Labtermo: Methodologies for the Calculation of the Corrected Temperature Rise in Isoperibol Calorimetry. *J. Therm. Anal. Calorim.* **2007**, *89*, 175–180.

(21) Good, W. D.; Scott, D. W.; Waddington, G. Combustion Calorimetry of Organic Fluorine Compounds by a Rotating-Bomb Method. *J. Phys. Chem.* **1956**, *60*, 1080–1089.

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

(23) Washburn, E. W. Standard States for Bomb Calorimetry. *J. Res. Natl. Bur. Stand. (U.S.)* **1933**, *10*, 525–558.

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

(25) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. Thermochemistry of Arene Chromium Tricarbonyls and Strengths of Arene–Chromium Bonds. *J. Organomet. Chem.* **1975**, *97*, 221–228.

- (26) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V. Measurement of Enthalpies of Sublimation by Drop Method in a Calvet Type Calorimeter: Design and Test of a New System. *Thermochim. Acta* **2004**, *415*, 15–20.
- (27) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of Sublimation of Organic and Organometallic Compounds. 1910–2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537–698.
- (28) Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D. New Static Apparatus and Vapor Pressure of Reference Materials: Naphthalene, Benzoic Acid, Benzophenone, and Ferrocene. *J. Chem. Eng. Data* **2006**, *51*, 757–766.
- (29) Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Santos, L. M. N. B. F. The design, construction, and testing of a new Knudsen effusion apparatus. *J. Chem. Thermodyn.* **2006**, *38*, 778–787.
- (30) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
- (31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (32) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. Gaussian-3 (G3) Theory for Molecules Containing First and Second-Row Atoms. *J. Chem. Phys.* **1998**, *109*, 7764–7776.
- (33) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. J. Gaussian-4 Theory. *J. Chem. Phys.* **2007**, *126*, No. 084108.
- (34) Good, W. D.; Scott, D. W. In *Experimental Thermochemistry*, Vol. 2; Skinner, H. A., Ed.; Interscience: New York, 1962; Chapter 2.
- (35) CODATA Key Values for Thermodynamics; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere: New York, 1989.
- (36) Clarke, E. C. W.; Glew, D. N. Evaluation of Thermodynamic Functions from Equilibrium Constants. *Trans. Faraday Soc.* **1966**, *62*, 539–547.
- (37) Chickos, J. S.; Hesse, D. G.; Liebman, J. F. A Group Additivity Approach for the Estimation of Heat Capacities of Organic Liquids and Solids at 298 K. *Struct. Chem.* **1993**, *4*, 261–269.
- (38) Monte, M. J. S.; Almeida, A. R. R. P.; Matos, M. A. R. Thermodynamic Study on the Sublimation of Five Aminomethoxybenzoic Acids. *J. Chem. Eng. Data* **2010**, *55*, 419–423.
- (39) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271–278.
- (40) Monte, M. J. S.; Sousa, C. A. D.; Fonseca, J. M. S.; Santos, L. M. N. B. F. Thermodynamic Study on the Sublimation of Anthracene-like Compounds. *J. Chem. Eng. Data* **2010**, *55*, 5264–5270.
- (41) Parsons, G. H.; Rochester, C. H.; Wood, C. E. C. Effect of 4-Substitution on the Thermodynamics of Hydration of Phenol and the Phenoxide Anion. *J. Chem. Soc. B* **1971**, 533–536.
- (42) de Kruif, C. G. Enthalpies of Sublimation and Vapour Pressures of 11 Polycyclic Hydrocarbons. *J. Chem. Thermodyn.* **1980**, *12*, 243–248.
- (43) Colomina, M.; Roux, M. V.; Turrion, C. Enthalpies of Combustion and Formation of the 1- and 2-Naphthols. *J. Chem. Thermodyn.* **1974**, *6*, 571–576.
- (44) Acree, W. E., Jr. Thermodynamic Properties of Organic Compounds: Enthalpy of Fusion and Melting Point Temperature Compilation. *Thermochim. Acta* **1991**, *189*, 37–56.
- (45) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* **2007**, *111*, 11683–11700.
- (46) Chase, M. W., Jr. NIST–JANAF Thermochemical Tables, 4th Edition. *J. Phys. Chem. Ref. Data*, Monograph 9, **1998**; pp 1–1951.
- (47) Notario, R.; Castaño, O.; Abboud, J.-L. M.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. Organic Thermochemistry at High ab Initio Levels. 1. A G2(MP2) and G2 Study of Cyclic Saturated and Unsaturated Hydrocarbons (Including Aromatics). *J. Org. Chem.* **1999**, *64*, 9011–9014.
- (48) Notario, R.; Castaño, O.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. Organic Thermochemistry at High ab Initio Levels. 3. A G3 Study of Cyclic Saturated and Unsaturated Hydrocarbons (Including Aromatics). *J. Org. Chem.* **2000**, *65*, 4298–4302.
- (49) Glukhovtsev, M. N.; Laiter, S. High Level ab Initio Stabilization Energies of Benzene. *Theor. Chim. Acta* **1995**, *92*, 327–332.
- (50) Minkin, V. I. Glossary of Terms Used in Theoretical Organic Chemistry. *Pure Appl. Chem.* **1999**, *71*, 1919–1981.
- (51) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. Accurate Thermochemistry for Larger Molecules: Gaussian-2 Theory with Bond Separation Energies. *J. Chem. Phys.* **1997**, *106*, 6764–6767.
- (52) Adkins, H.; Eloffson, R. M.; Rossow, A. G.; Robinson, C. C. The Oxidation Potentials of Aldehydes and Ketones. *J. Am. Chem. Soc.* **1949**, *71*, 3622–3629.