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The effect of halogen hetero-atoms on the vapor pressures and thermodynamics of polycyclic aromatic compounds measured via the Knudsen effusion technique

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Abstract

Knowledge of vapor pressures of high molar mass organics is essential to predicting their behavior in combustion systems as well as their fate and transport within the environment. This study involved polycyclic aromatic compounds (PACs) containing halogen hetero-atoms, including bromine and chlorine. The vapor pressures of eight PACs, ranging in molar mass from (212–336) $g \cdot mol^{-1}$, were measured using the isothermal Knudsen Effusion technique over the temperature range of (296–408) K. These compounds included those with few or no data available in the literature, namely: 1,4-dibromonaphthalene; 5-bromoacenaphthene; 9-bromoanthracene; 1,5-dibromoanthracene; 9,10-dibromoanthracene; 2-chloroanthracene; 9,10-dichloroanthracene and 1-bromopyrene. Enthalpies of sublimation of these compounds were determined via application of the Clausius-Clapeyron equation. An analysis is presented on the effects of the addition of halogen hetero-atoms to pure polycyclic aromatic hydrocarbons using these data as well as available literature data. As expected, the addition of halogens onto these PACs increases their enthalpies of sublimation and decreases their vapor pressures as compared to the parent compounds.

Keywords

vapor pressure; polycyclic aromatic hydrocarbons; halogen; hetero-atom; Knudsen effusion

1. Introduction

A variety of applications requires vapor pressure data for predicting many phenomena; *e.g.* the pharmaceutical industry uses vapor pressures in developing inhalation delivery systems and for estimating the potential hazards associated with the inhalation of toxic vapors [1]. The vapor pressures of polycyclic aromatic compounds (PACs) are important in flame modeling [2] and in determining thermal remediation conditions for sites contaminated with coal and other fossil fuels, such as former manufactured gas plants [3]. There exist relatively few vapor pressure and thermodynamic data concerning PACs.

This study focused on those PACs containing chlorine and bromine atoms, persistent organic pollutants (POPs) included in many toxic risk assessments [4]. Polycyclic aromatic hydrocarbons are found at processing sites for fossil fuels. The PAHs may undergo a variety of halogenation mechanisms to yield PACs in various processes of their environments. For example, Hu *et al.* [5] show that the presence of bromine ions significantly increases the reaction rate of the cholorination of pyrene, while simultaneously producing brominated pyrenes, including 1-bromopyrene. The promotion of soot formation in flames by chlorine and chlorinated hydrocarbons is linked to PAH formation, as PAHs are believed to be soot precursors [6]. In the presence of bromine and chlorine, it may be possible to promote the formation of halogenated and non-halogenated PAHs [5].

A further step in this research was to analyze available literature data on halogenated PACs in conjunction with the newly obtained data set to investigate whether trends exist with the substitution of halogens onto these environmentally critical aromatic compounds. An extensive literature exists on group contribution methods for predicting phase equilibrium for organic compounds, yet many of these models fall short when polycyclic aromatics are considered [7]. Thus, we aim towards a future ability to describe, systematically, the thermodynamic effect of halogen substitution on the vapor pressures of PACs, for which the presently reported data would be very valuable.

To perform this work, we use the Knudsen effusion technique, which enables the measurement of vapor pressures of high molar mass, semi-volatile organic compounds indirectly via the molecular effusion of a vapor through an orifice under a high vacuum at low to moderate temperatures. This technique eliminates the need for the high temperatures required to measure low volatility compound vapor pressures directly, as high temperatures result in the thermal degradation of these compounds.

The Knudsen effusion method is used to determine indirectly vapor pressures by measuring the molecular leak rate from an effusion cell through a small orifice, without disturbing the thermal and chemical equilibrium within the cell. Application of the Knudsen theory stipulates the conditions of thermal and chemical equilibrium within the sample cell. The rate of molecular effusion through the pinhole leak (measured as the mass loss of sample from the cell) equals the rate at which molecules would strike an area of wall equal to the area of the hole, if the hole were not present; the long mean free path of the vapor molecules as compared to the radius of the orifice justifies this assumption. The use of high vacuum ($<10^{-7}$ Torr) guarantees this required long mean free path, enabling measurements of vapor pressures as low as 10^{-6} Torr, at experimental temperatures sufficiently low enough to prevent thermal degradation of the sample. The vapor pressures measured are actually sublimation vapor pressures because of the low temperatures and solid state of the polycyclic aromatic compounds examined. By assuming a constant enthalpy of sublimation, $\Delta_{sub}H$, over the temperature ranges employed, the Clausius-Clapeyron equation models the vapor pressure data as a function of temperature:

$$\ln P^{\circ} = -\Delta_{sub}H/RT + \Delta_{sub}S/R, \qquad (1)$$

where P° is the saturation vapor pressure, T is the absolute temperature, $\Delta_{sub}S$ is the entropy of sublimation, and R is the universal gas constant. This integrated form of the Clausius-Clapeyron equation results in a fairly linear vapor pressure curve of ln P° vs. 1/T, well representing data in the pressure region of 10^{-6} to 10^{-3} Torr.

2. Experimental

2.1. The Knudsen Effusion Technique

The present implementation of the Knudsen effusion method is described in previous publications [3,8]. Measurements were made under isothermal conditions, using an Omega type K thermocouple, calibrated to ±0.1K, located directly above the effusion cell opening. The cell was suspended on one arm of a Cahn 2000 microbalance with a sensitivity of 0.5μg and hangs inside a black copper capsule within the glass-enclosed thermo-gravimetric apparatus (TGA). The balance is interfaced with a National Instruments Data Acquisition Board recording a signal into a National Instruments Labview 7.0 program, continuously monitoring the mass loss and temperature as a function of time. A BOC Edwards turbo-molecular pump maintains the backpressure in the TGA at 10^{-8} Torr. A Stanford Mass Spectrometer is located after the effusion cell opening to measure the composition of the effusing vapor, used to ensure there is no degradation of the sample and to check the purity of the compounds. A condenser slightly downstream of the mass spectrometer opening helps maintain the high vacuum outside of the cell.

2.2. Materials Examined

For each compound examined, vapor pressure results were confirmed by a minimum of two independent sets of measurements, in two different effusion cells, to ensure reproducibility. The polycyclic aromatic compounds examined range in molar mass from (212–336) $g{\cdot}mol^{-1}$, and were all obtained from TCI America at a minimum purity of 94%. The compounds were placed into the effusion cells straight from the supply container; at least 6% (by mass) of each compound was sublimed before commencing data collection to ensure removal of any volatile impurities, and data recording halted with at least 6% (by mass) remaining to account for any nonvolatile impurities. This method was confirmed by the use of the mass spectrometer to measure the spectra of the effusing vapor. Figure 1, below, shows the spectra of 1-bromopyrene after approximately 1% mass loss and again at 6% mass loss. From these data, we conclude that the fractional sublimation is sufficient to remove the impurities present in the compounds; the impurities all appear to be more volatile than the compound under investigation. These measurements were taken for the four least pure compounds: 5-bromoanthracene, 9-bromoanthracene, 9,10-dichloroanthracene, and 1-bromopyrene. For each compound, the least volatile impurity measured was at the mass of the parent aromatic compound (at 202 atomic mass units for 1-bromopyrene, the mass of the parent compound, pyrene, and so on.) After 6% of the mass was sublimed for each compound, at both the high and low temperatures measured for each compound, over 99% of the vapor phase composition from that point was the halogenated PAH, with the balance hydrogen, nitrogen and oxygen. Furthermore, the melting points of the four least pure compounds were measured using a Digimelt capillary melting point apparatus, for which all fell within their reported literature range; for example, the supplier reports a melting point for 9,10-dichloranthracene of $T = 483$ K, which we measured at $T = 482.53$ K, suggesting that any impurities present are likely volatile in nature. This was confirmed for the three other compounds.

3. Results

The experimental technique was validated by comparing vapor pressures obtained using the present technique applied to fluorene, anthracene, and pyrene, and comparing these to available literature values, spanning a temperature range of 298K to 381K [8].

Table 1 presents data obtained using isothermal steps. These data were examined using the Knudsen effusion equation (equation 1, above) to obtain the enthalpies and entropies of sublimation of each compound, displayed in table 2, which also details the statistical significance of these results; a 95% confidence interval was calculated for each set of experimental results using linear regression.

Figures 2 through 5 demonstrate the effects of the addition of halogen hetero-atoms on the vapor pressures of parent PACs. We begin by examining the effect on the enthalpy of sublimation with the substitution of chlorine and bromine onto naphthalene, for which the parent enthalpy of sublimation falls around 73.3 $kJ{\bullet}mol^{-1}$ over the temperature range of 258K to 314K [10]. The enthalpy of sublimation of 2-bromonaphthalene measured by Ribeiro da Silva, Ferrão and Lopes [11] was (81.2 ± 1.0) $kJ{\bullet}mol^{-1}$ at $T = (280–328)$ K, in good accord with that (80.4 ± 0.68 $kJ{\bullet}mol^{-1}$) measured by Verevkin [12]. These data show an increase in enthalpy of approximately 10% (or 7 to 8 $kJ{\bullet}mol^{-1}$) with the substitution of a single bromine onto the

2-position of naphthalene. Our measured value for the enthalpy of sublimation of 1,4-dibromonaphthalene is (90.8±1.7) kJ•mol^{-1}, an increase of 17.5•kJ mol^{-1}, or about 24% over pure naphthalene; thus, we note that the effect of each bromine substituent is in the range of (7–10) kJ•mol^{-1}. Verevkin measured the enthalpy of sublimation of 2-chloronaphthalene as (75.5±0.631) kJ•mol^{-1}, showing a very slight increase as compared to the parent naphthalene [11]. Figure 2 illustrates these observations in a Clausius-Clapeyron plot.

The same trend is observed with the addition of one chlorine to anthracene, creating 2-chloroanthracene; we measured the enthalpy of sublimation at (99.3± 2.6) kJ•mol^{-1}, compared to pure anthracene {ΔH_{sub}=(98.5±3.3) kJ•mol^{-1}, [8]}. The sublimation enthalpy showed very little change upon substitution as seen in figure 3. With the addition of two chlorines, the enthalpy of sublimation of 9,10-dichloranthracene is measured at 113.9± kJ•mol^{-1}, an increase of approximately 14%, or 15.4 kJ•mol^{-1} from the parent molecule.

We see only a slightly higher enthalpy of sublimation for 1,5-dibromoanthracene and 9,10-dibromoanthracene at 116.7±3.0 kJ•mol^{-1} and 114.2±2.7 kJ•mol^{-1}, respectively than for the 9,10-dichloroanthracene at 113.9±1.5 kJ•mol^{-1}, even though bromine is a significantly larger atom than chlorine (refer to table 2). It does not appear that the position of the halogens on the dibrominated anthracenes alters the enthalpy of sublimation to a statistically significant degree, as illustrated in figure 4. Again in this case, the addition of a single bromine atom to anthracene does not appear to influence the enthalpy of sublimation very much.

For pyrene, a four-ring PAC, the addition of one bromine atom does not change the measured enthalpy of sublimation by a significant amount, as may be seen in table 2. The vapor pressure of 1-bromopyrene was notably lower than for unsubstituted pyrene, as shown in figure 5.

The vapor pressure of acenaphthene was significantly lowered by the addition of a single bromine atom, decreasing by almost a full order of magnitude at room temperature. In this case, the substituted acenaphthene shows a higher enthalpy of sublimation than did the unsubstituted (87.4±2.6) kJ•mol^{-1} compared to (78.7±2.2) kJ•mol^{-1}).

4. Discussion

Overall, the successive addition of halogens to polycyclic aromatic compounds always decreases the vapor pressure as compared to the unsubstituted compound. As expected, the more halogens substituted, the lower the vapor pressure. Single chlorine substitution had a significantly smaller effect on vapor pressure than did bromine substitution at the same position for naphthalene, even though the enthalpy of sublimation was not much influenced by the chlorine heteroatom. The vapor pressure at T = 298 K for 2-chloronapthalene was measured by Verevkin to be 2.49 Pa, compared to 0.84 Pa for 2-bromonaphthalene. For anthracene at the same temperature, two bromines at the 9,10 positions yielded a vapor pressure of $3.68*10^{-6}$ Pa and two chlorines at the same positions of $2.17*10^{-5}$ Pa.

In the case of the smaller naphthalene, the difference in vapor pressures appears to be due more to enthalpic considerations, whereas for the larger anthracene, the difference is more attributable to entropic effects. One observable trend among the PACs composed of only fused benzene rings (naphthalene, anthracene and pyrene) is that the relative effect of halogen addition decreases as the parent compound’s molecular size increases; the change in enthalpy of sublimation with the addition of one bromine increases in naphthalene by +7.1kJ·mol^{-1}, in anthracene by 2.0kJ·mol^{-1} and in pyrene by 1.4 kJ·mol^{-1}. The addition of one bromine to acenaphthene causes an increase in the ΔH_{sub} by 8.7 kJ·mol^{-1}, comparable to that in naphthalene.

In all instances, the hetero-atom substitution decreased the vapor pressure compared to the parent compound. The magnitude of the effect was, however, not always easily predictable based upon the above observations. For example, addition of a single bromine to anthracene had a much more modest effect on vapor pressure than did addition of a single bromine to either the smaller naphthalene or the larger pyrene. In naphthalene, the reduction is almost purely of enthalpic origin. For pyrene, the entropic change is larger for the unsubstituted than for the substituted compound. In the intermediate anthracene case, neither the enthalpic nor entropic effects are large; the vapor pressure is not significantly influenced by the single substitution.

From these data, we conclude that the effect of a single bromine or chlorine substitution decreases as the parent molecule increases in size. In addition, we only see a significant difference in the change in enthalpy of sublimation with the addition of a single bromine atom versus one chlorine for naphthalene, the smallest of the PACs measured. The difference in enthalpy between substituting either chlorine or bromine onto anthracene or pyrene was significantly smaller. Larger thermodynamic effects occur with the addition of two halogens, though it appears from the dibrominated anthracenes that the carbon position to which the halogens are substituted does not strongly influence the change in vapor pressure.

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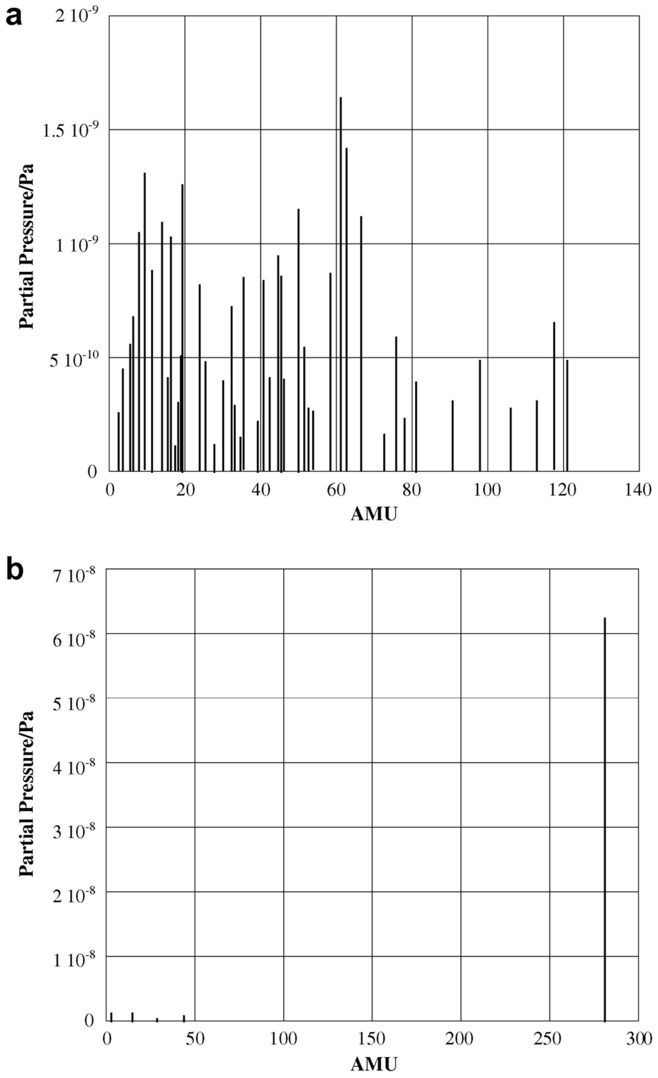


Figure 1.

a: Mass spectrum of 1-bromopyrene following 1% mass loss with multiple low-volatile impurities. **B:** Mass spectrum of 1-bromopyrene following 6% mass loss yielding only 1-brompyrene, hydrogen, nitrogen and oxygen and water.

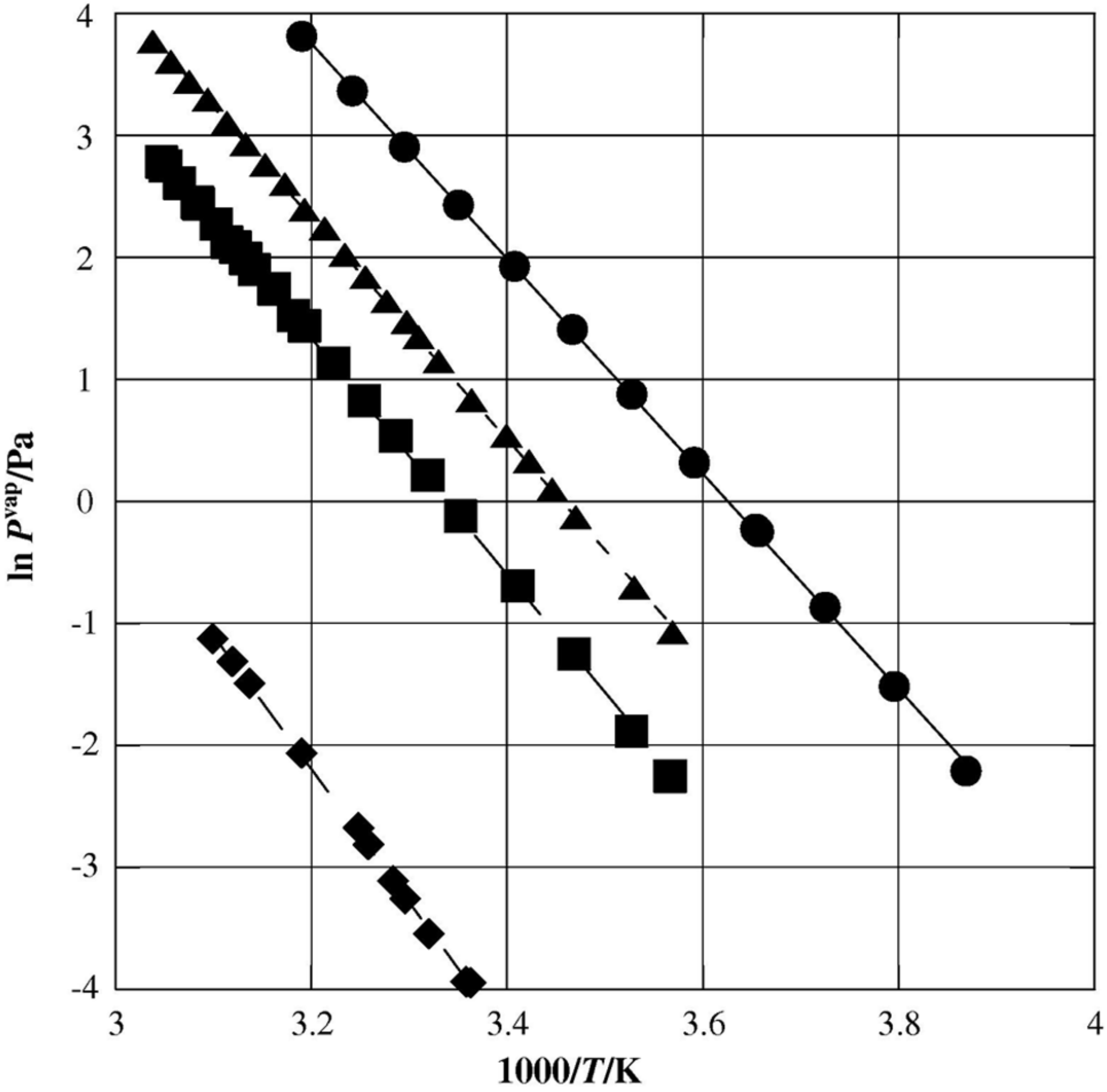


Figure 2.
Plot of sublimation vapor pressures against reciprocal temperature for the halogenated naphthalenes; λ naphthalene [10] ν 2-bromonaphthalene [12] υ 1,4-dibromonaphthalene (this study); σ 2-chloronaphthalene [12]

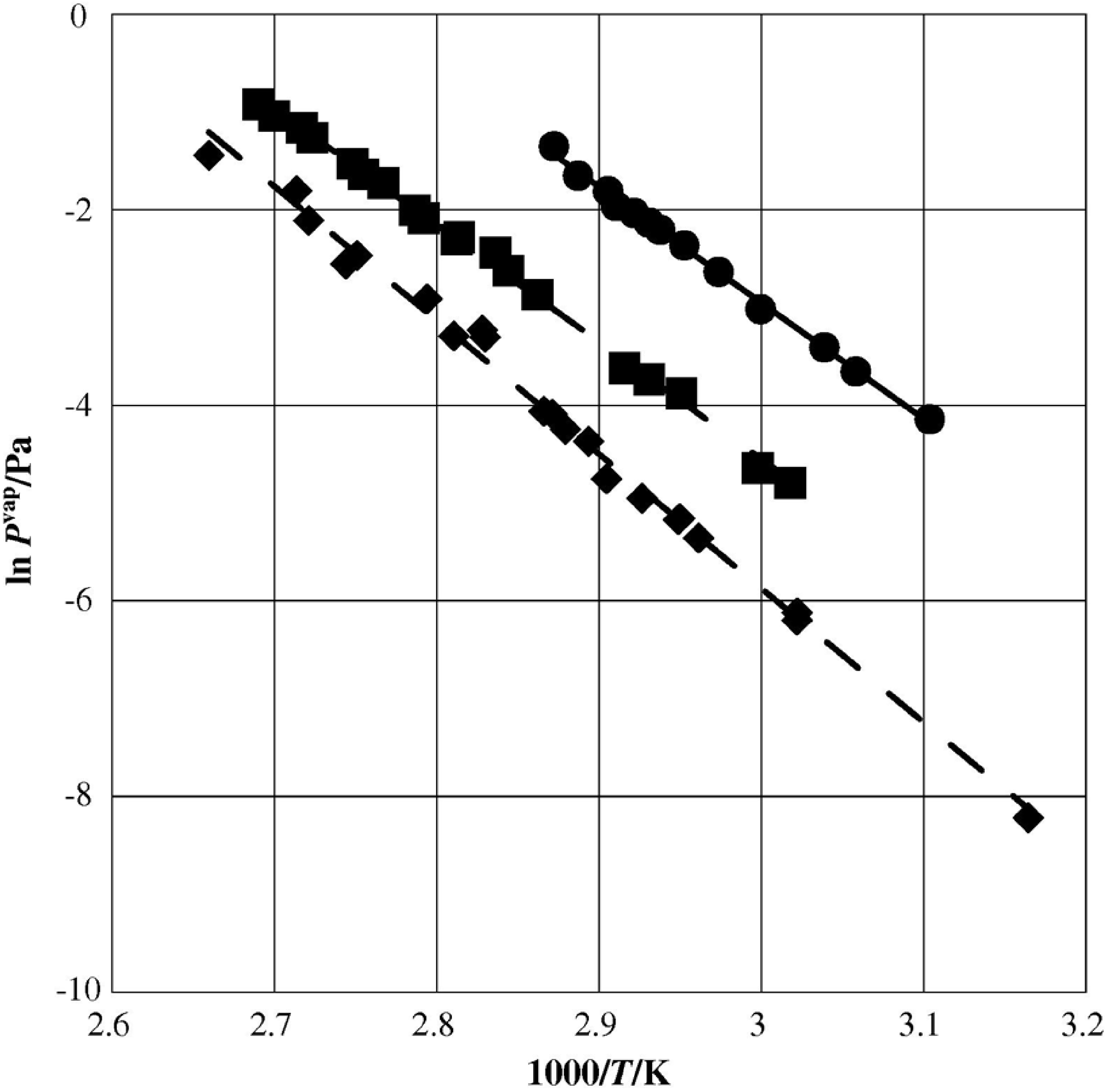


Figure 3.
Plot of sublimation vapor pressures against reciprocal temperature for chlorinated anthracenes as measured by the Knudsen effusion technique; λ anthracene [9]; ν 2-chloroanthracene; ◆ 9,10-dichloroanthracene

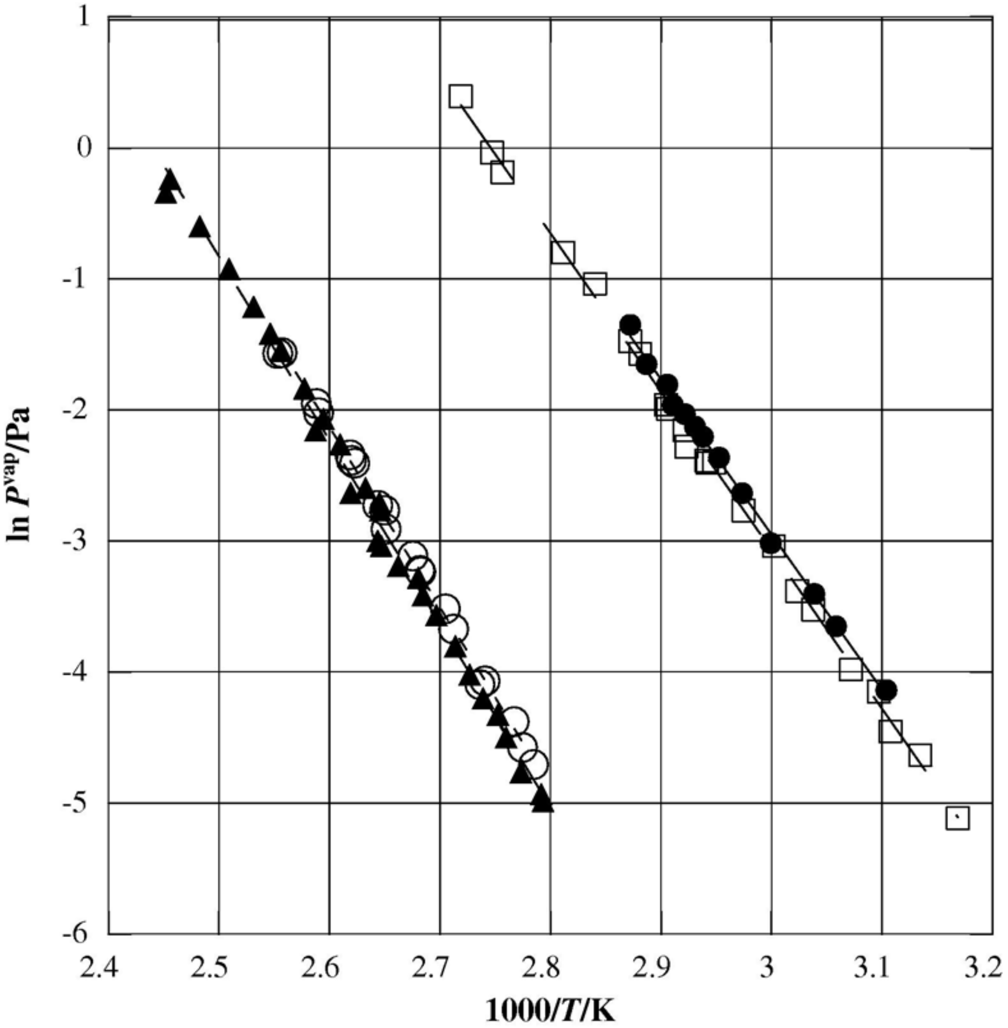


Figure 4.

Plot of sublimation vapor pressures against reciprocal temperature for brominated anthracenes as measured by the Knudsen effusion technique; λ anthracene [9]; θ 9-bromoanthracene; σ 1,5-dibromoanthracene; μ 9,10-dibromoanthracene

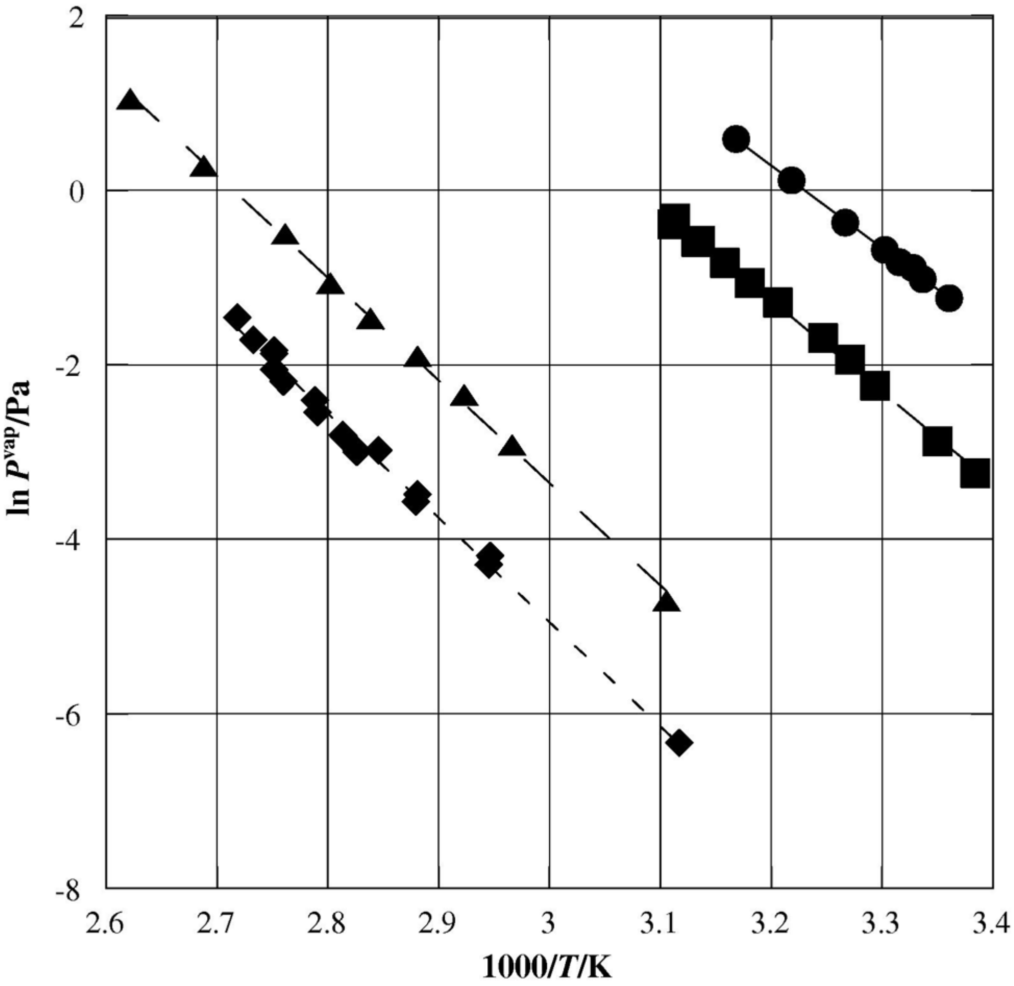


Figure 5.

Plot of sublimation vapor pressures against temperature for 5-bromoacenaphthene and 1-bromopyrene compared to parent PAHs determined via the Knuden effusion technique; λ acenaphthene [8]; ν 5-bromoacenaphthene; σ pyrene[9]; υ 1-bromopyrene.

Table 1

Measured vapor pressures of halogenated PACs

1,4-dibromonaphthalene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
297.4	0.0193	307.9	0.0688
297.8	0.0195	313.5	0.127
301.2	0.0288	318.8	0.225
303.4	0.0384	320.6	0.269
304.6	0.0445	322.7	0.325
306.9	0.0599		

5-bromoacenaphthene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
295.5	0.0392	314.4	0.344
298.5	0.0563	316.6	0.435
303.6	0.107	318.9	0.560
305.7	0.144	319.2	0.553
308.0	0.184	321.2	0.725
311.9	0.277	321.4	0.679

9-bromoanthracene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
315.6	0.0060	342.1	0.102
319.0	0.0097	342.3	0.116
321.8	0.0116	344.1	0.136
322.9	0.0157	344.3	0.141
325.5	0.0187	347.1	0.208
329.2	0.0295	348.2	0.229
330.8	0.0340	352.1	0.353
333.1	0.0479	355.7	0.450
336.2	0.0628	362.8	0.830
339.2	0.0905	364.0	0.966
339.9	0.0904	367.8	1.48
340.0	0.0919		

1,5-dibromoanthracene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
358.0	0.0068	378.3	0.050
358.2	0.0072	379.8	0.0746
360.6	0.0085	381.8	0.0718
362.3	0.0112	383.2	0.1041
363.3	0.0133	385.4	0.1269
365.1	0.015	386.5	0.1162
366.7	0.018	388.0	0.1593

368.5	0.0223	391.2	0.2126
370.8	0.0283	392.7	0.2427
372.5	0.033	395.0	0.2976
373.1	0.0376	398.5	0.3977
375.6	0.0412	402.8	0.5508
377.8	0.048	407.2	0.7873
377.9	0.0631	407.8	0.710
378.0	0.0668		

9,10-dibromoanthracene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
359.1	0.0090	377.2	0.0546
360.4	0.0103	377.4	0.0630
361.4	0.0126	378.3	0.0655
364.9	0.0171	381.3	0.0905
365.5	0.0167	381.7	0.0923
368.7	0.0255	381.9	0.0964
369.7	0.0297	386.1	0.133
372.8	0.0394	386.4	0.142
372.9	0.0399	391.1	0.210
373.8	0.0445	391.7	0.208

2-chloroanthracene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
331.4	0.0083	358.2	0.124
333.6	0.0097	358.9	0.135
338.9	0.0208	361.4	0.179
341.2	0.0240	363.0	0.195
343.0	0.0270	363.9	0.217
349.4	0.0571	367.2	0.284
351.6	0.0729	368.1	0.314
352.6	0.0876	370.4	0.355
355.4	0.103	371.8	0.400
355.6	0.100		

9,10-dichloroanthracene

T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
316.0	2.7E-04	348.9	0.0172
330.8	0.0020	353.4	0.0370
330.9	0.0022	353.6	0.0394
337.7	0.0047	355.8	0.0374
339.1	0.0057	357.9	0.0546
341.7	0.0071	363.5	0.0847
344.3	0.0087	364.4	0.0779
345.6	0.0127	367.5	0.1216

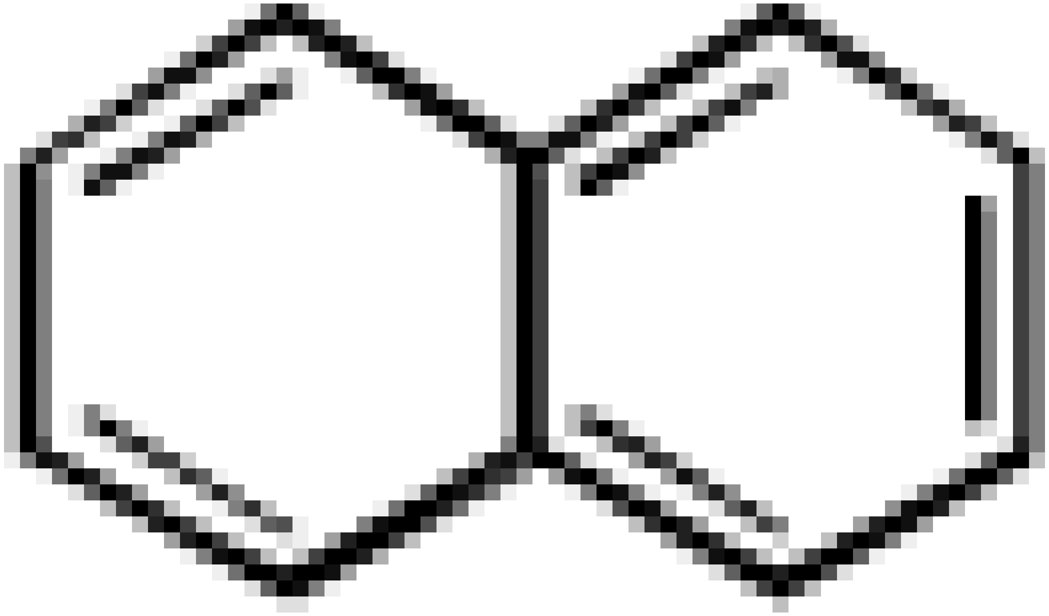
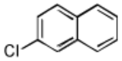
347.3	0.0144	368.5	0.1645
348.3	0.0167	376.0	0.2362

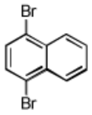
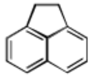
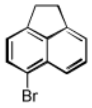
1-bromopyrene

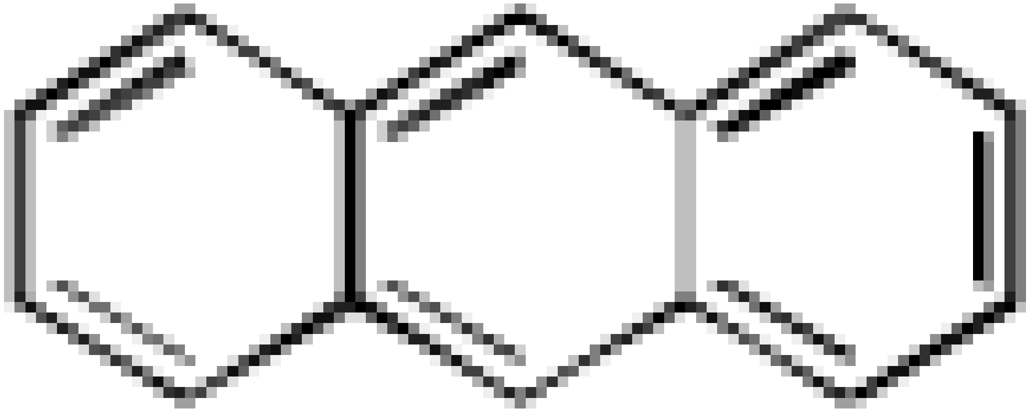
T/K	P^{vap}/Pa	T/K	P^{vap}/Pa
320.8	0.0018	355.4	0.0606
339.4	0.0152	358.3	0.0783
339.5	0.0137	358.6	0.0901
347.1	0.0308	362.3	0.112
347.3	0.0282	363.4	0.155
351.4	0.0508	363.4	0.128
353.8	0.0508	363.4	0.160
353.8	0.0497	365.9	0.180
355.3	0.0594	367.9	0.233

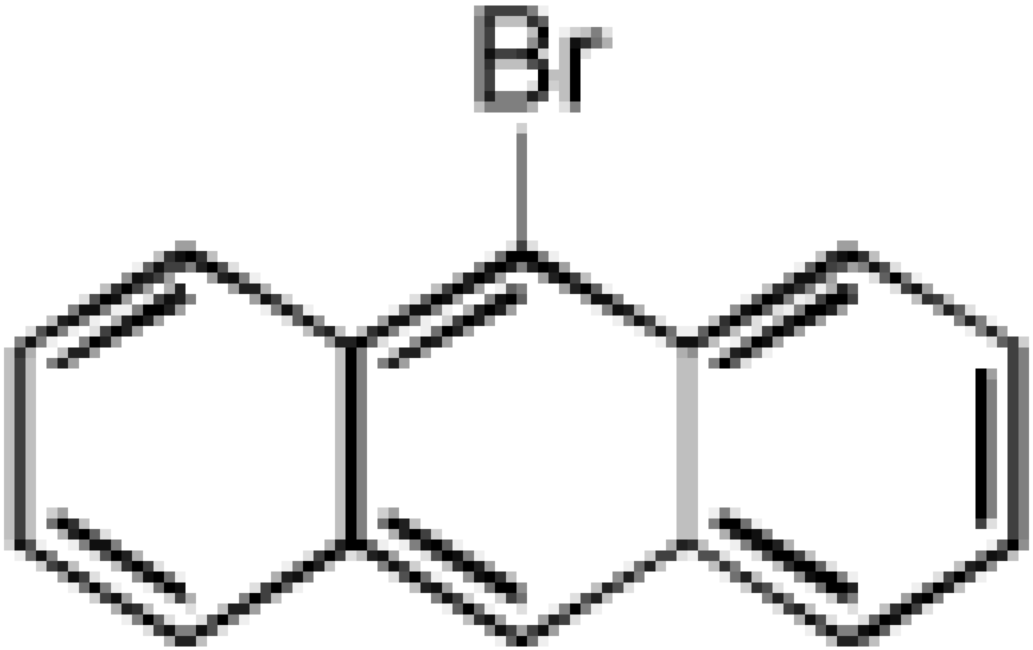
Table 2

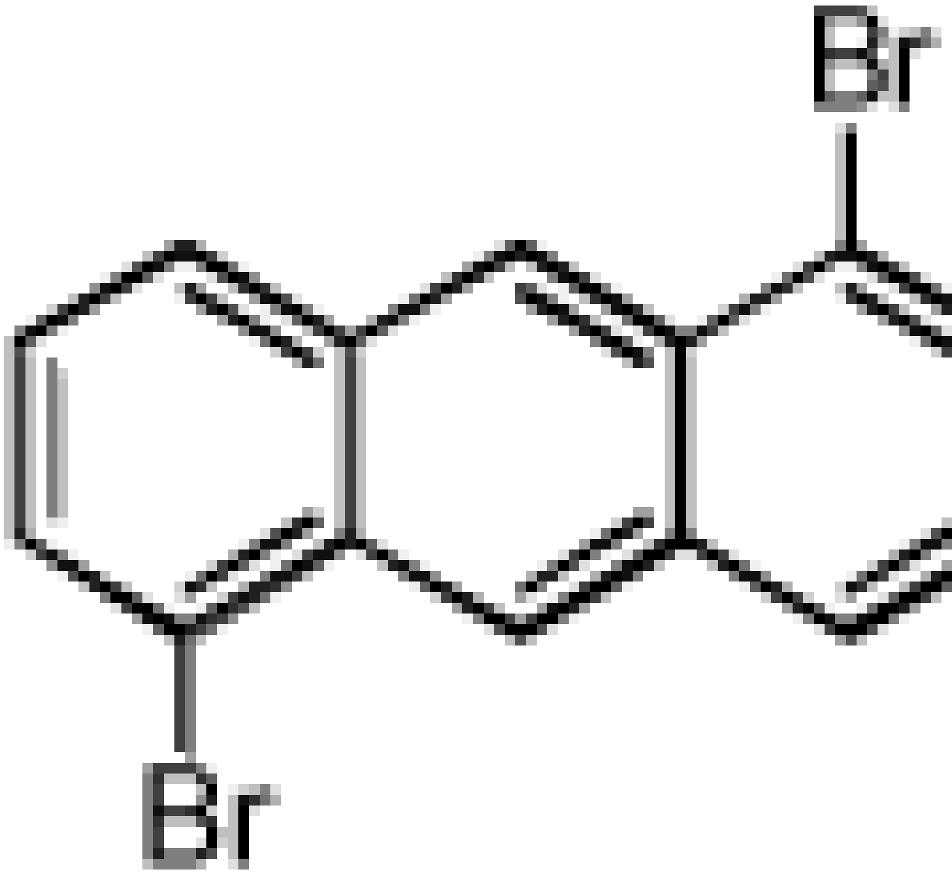
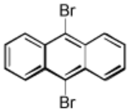
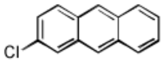
of halogenated PACs as determined via the Clausius-Clapeyron equation.

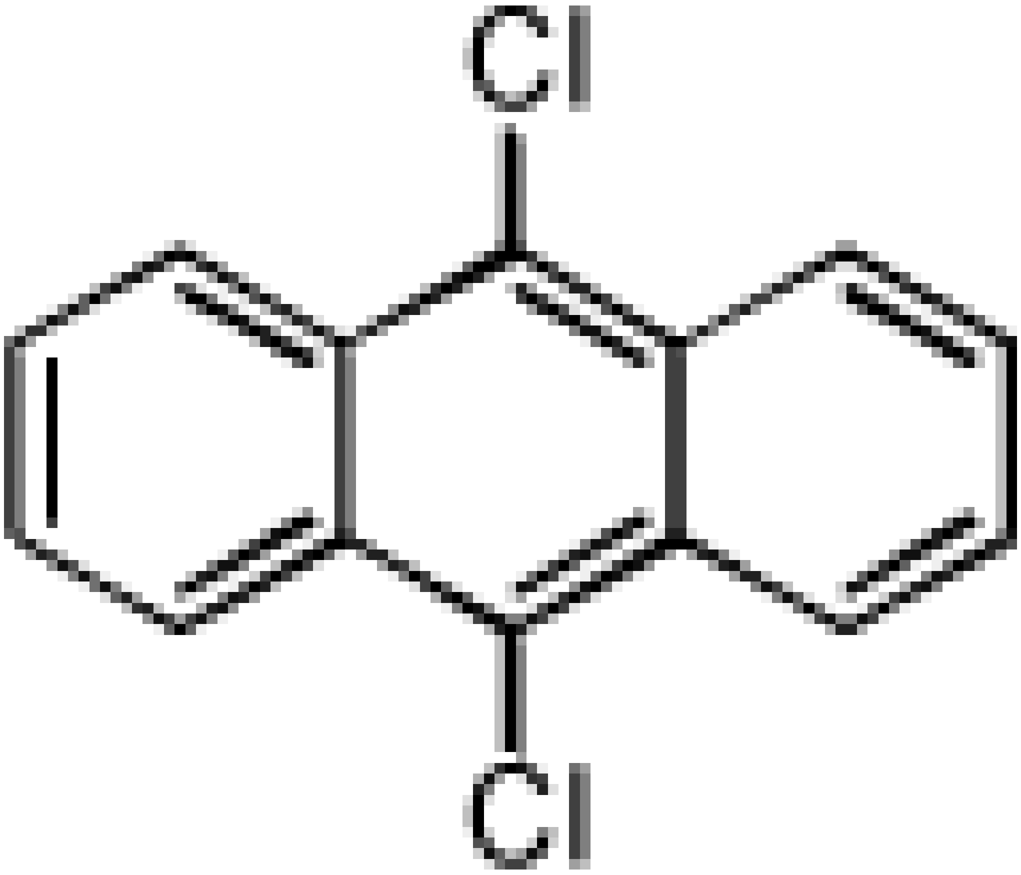
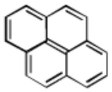
Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub} H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ $K^{-1}mol^{-1}$	Molecular Structure
128.17	>99	258–314	73.3± 0.61	0.266	
162.62	>99	280–329	75.5 ± 0.63	0.261	

Molecular Weight g mol^{-1}	**Min. Purity %**	**Temp Range K**	**$\Delta_{sub}H$ kJ mol^{-1}**	**$\Delta_{sub}S$ kJ K^{-1}mol^{-1}**	**Molecular Structure**
207.07	>99	280–328	80.4 ±0.68	0.268	
285.96	98	297–322	90.8 ± 1.7	0.272	
154.21	99	299–320	78.7 ± 2.2	0.254	
233.10	>94	296–321	87.4 ± 2.6	0.269	

Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub}H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ K^{-1}mol^{-1}	Molecular Structure
178.23	99	322–348	98.5 ± 3.3	0.271	

.	Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub}H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ K^{-1}mol^{-1}	Molecular Structure
	257.13	95	316–368	100.5 ± 1.8	0.276	

Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub}H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ K^{-1}mol^{-1}	Molecular Structure
336.02	98	358–408	116.7 ± 3.0	0.285	
336.02	98	359–392	114.2 ± 2.8	0.279	
212.67	>98	331–372	99.3 ± 2.7	0.260	

.	Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub} H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ K^{-1}mol^{-1}	Molecular Structure
	247.12	>96	316–376	113.9 ± 4.5	0.293	
	202.26	99	322–381	97.8 ± 3.3	0.266	

.	Molecular Weight g mol^{-1}	Min. Purity %	Temp Range K	$\Delta_{sub} H$ kJ mol^{-1}	$\Delta_{sub}S$ kJ K^{-1}mol^{-1}	Molecular Structure
	281.15	94	321–366	99.2 ± 4.3	0.257