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The enthalpy of vaporization and sublimation of corannulene, coronene, and perylene at $T = 298.15$ K

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The sublimation enthalpy of corannulene $\Delta_{cr}^{g}H_m$ (298.15 K) has been measured by head space analysis and by combining the fusion and vaporization enthalpies. A mean value of (118.3 ± 3.3) kJ·mol^{-1} was obtained. The vaporization enthalpies of perylene and coronene were also measured by correlation gas chromatography. Combining the vaporization enthalpy of perylene with the fusion enthalpy adjusted to $T = 298.15$ K affords a sublimation enthalpy at 298.15 K of (138.1 ± 6.2) kJ·mol^{-1}. This value permits a distinction to be made between several discordant sublimation enthalpies in the literature. The vaporization enthalpy of coronene measured in this work permits an identification of the most probable sublimation enthalpy value among a series of varying literature values. A value of (155 ± 7.0) kJ·mol^{-1} is recommended for $\Delta_{cr}^{g}H_m$ (298.15 K) of coronene. The new data reported here complete the experimental determination of gas-phase enthalpy of formation values, $\Delta_f H_m^o$ (g, 298.15 K): for corannulene (460.6 ± 6.5) kJ·mol^{-1}, perylene (319.4 ± 2.2) kJ·mol^{-1}, and coronene (307.5 ± 9.8) kJ·mol^{-1}.

1. Introduction

The strain and resonance energies of fullerenes, the new spherical allotropic forms of carbon, corannulene, a bowl-shaped $C_{20}H_{10}$ hydrocarbon, and of coronene, a planar

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$C_{24}H_{12}$ polycyclic aromatic hydrocarbon, have been of considerable interest in recent years.[1–3] Enthalpies of formation of the solids have been determined by combustion calorimetric measurements.[2, 4] This work reports the experimental enthalpies of sublimation of corannulene and perylene and provides a reasonable method of assessing the enthalpy of sublimation of coronene. The structures of the compounds studied in the present work are shown in figure 1.

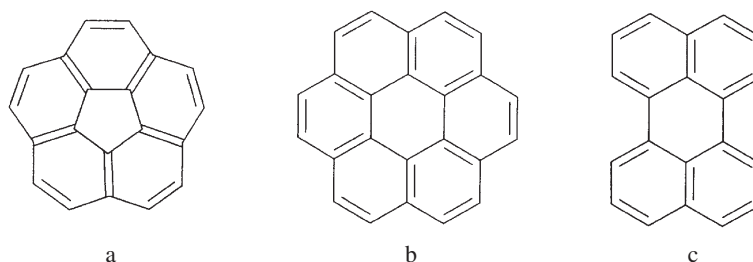   a   b   c

FIGURE 1. Structures of: a, Corannulene; b, coronene; c, perylene.

The sublimation enthalpy of corannulene has been determined by measurement of vapor pressure as a function of temperature by head space analysis. The sublimation enthalpies of corannulene, coronene, and perylene have also been measured from the sum of the vaporization and fusion enthalpies adjusted for temperature to $T = 298.15$ K. The vaporization enthalpies of these samples have been obtained by means of correlation-gas chromatography.[5, 6] The gas-phase enthalpies of formation of corannulene and perylene are evaluated, and the most probable experimental value for the enthalpy of sublimation of coronene is provided. The results are compared with theoretical calculations reported previously.

2. Experimental

Coronene (mass fraction, 0.99) and perylene (mass fraction, 0.995) were obtained from Aldrich Chem. Co. The corannulene, prepared as reported previously,[7] had a mass fraction purity of >0.99 according to gas chromatographic analysis. Sublimation enthalpies were evaluated by means of head space analysis as described previously.[8] Vapor pressures p were calculated by applying the ideal gas law to the mass of solute condensed from a ballast tank with a volume of 12.4 dm^3. The mass of solute was determined by u.v. analysis on a dual beam Hitachi spectrophotometer. Values of sublimation enthalpy evaluated by head space analysis are usually accurate to within a few percent and have a tendency to be slightly lower than those measured by other methods. Absolute vapor pressures are generally not considered highly accurate because of adsorption effects and some caution is recommended in using them. Sample temperatures in table 1 are accurate to within ±0.2 K.

Correlation gas chromatography experiments were performed on an HP 5890 Series II Gas Chromatograph equipped with a (split, splitless) capillary injection port and a flame ionization detector. Retention times were recorded to three significant figures following the decimal point on a HP 3989A integrator. The instrument was run isothermally with

TABLE 1. Vapor pressure p results for corannulene by head space analysis. The temperature of the sample is denoted by T

p/Pa	T/K	p/Pa	T/K
0.093	390.55	0.460	409.05
0.106	391.35	0.690	414.35
0.111	392.15	0.704	414.45
0.200	398.75	0.788	414.45
0.202	398.35	0.976	419.45
0.296	403.45	1.06	419.45
0.297	403.35	1.09	419.45
0.270	403.25	1.68	425.15
0.417	409.05	1.64	425.15
0.426	409.05	1.64	425.15

different columns that included a 12 m HP-1 column and a 30 m SPB-5 capillary column. At the temperatures of the experiments, the solvent was not retained; the retention times of the solvent were used to determine the dead volume of the column. Corrected retention times t_{rc} were calculated by subtracting the measured retention time of each analyte from the retention time of the solvent as a function of temperature over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. Temperature was maintained constant to ± 0.2 K. The literature values used for the n-alkanes C_{18} to C_{20} are those recommended by Ružicka and Majer[9] and for the n-alkanes C_{22} to C_{28} are those recommended by Chickos and Wilson.[10] The purities of the standards are not particularly relevant here since the chromatography generally separates the impurities, and the standards are analyzed as a mixture. The purity of the standards generally had a mass fraction purity of 0.99 or better. Uncertainties are reported as two standard deviations unless noted otherwise.

Fusion enthalpies were measured on a Perkin Elmer DSC 7. Measurements were conducted in triplicate under nitrogen at a temperature scan rate of 0.0833 K $\cdot$ s^{-1}. The samples were hermetically sealed in stainless steel capsules. The instrument was standardized by using the fusion enthalpy of indium, and checked by using the fusion enthalpies of biphenyl, naphthalene, and benzoic acid.[11] The uncertainty $(\pm 2 \cdot \sigma)$ associated with the use of equation (4) has arbitrarily been chosen as one-third of the total temperature adjustment.

3. Results and discussion

Vapor pressure measurements for corannulene are reported in table 1. Equation (1) resulted from a non-linear least squares treatment of the data at the mean temperature indicated

$(\langle T \rangle = 408$ K$)$:

$$\ln(p/\text{Pa}) = 33.18 - 13891 \cdot (\text{K}/T). \tag{1}$$

The vapor pressure of coronene was too small to measure directly by head space analysis. Vaporization enthalpies were evaluated by measuring the retention times of a mixture of hydrocarbons as a function of temperature. A total of five mixtures of various standards and test compounds were prepared, and their relative retention times were compared. The results are presented in table 2.

Enthalpies of transfer from solution to the vapor were measured for corannulene, coronene, perylene, and an additional eight standards. The results are reported in table 3. Each enthalpy was derived from the slope of the line obtained by plotting lgt_{re} against $1/T$. The enthalpies of transfer of the standards were then correlated against their respective enthalpies of vaporization at $T = 298.15$ K. The vaporization enthalpies of the standards used in the correlations are reported in the second column of table 4. Measurements were conducted over a range of temperature. The mean temperatures of a series of five different mixtures are reported at the top left of table 3 under each respective run. A typical plot of vaporization enthalpy against enthalpy of transfer and the corresponding correlation equation are given in figure 2 for run 5. The vaporization enthalpies calculated from each correlation equation are listed in columns 7 to 11 of table 3. The uncertainties were generated from the standard error in the slope. Table 4 summarizes vaporization enthalpies from the literature and those obtained in this study for both standard and target molecules. The uncertainty represents two standard deviations of the mean.

Enthalpies of sublimation, vaporization, and fusion measured at other temperatures were adjusted to $T = 298.15$ K by means of equations (2) to (4) according to the protocol described elsewhere.[12–14]

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}\langle T \rangle + \{0.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} +$$
$$0.15 \cdot C_{p,\text{m}}(\text{cr})\} \cdot \{\langle T \rangle - 298.15 \text{ K}\}, \tag{2}$$

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}\langle T \rangle + \{10.58 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} +$$
$$0.26 \cdot C_{p,\text{m}}(\text{cr})\} \cdot \{\langle T \rangle - 298.15 \text{ K}\}, \tag{3}$$

$$\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}\langle T_{\text{fus}} \rangle + \{0.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} +$$
$$0.15 \cdot C_{p,\text{m}}(\text{cr})\} \cdot \{\langle T \rangle - 298.15 \text{ K}\} -$$
$$\{10.58 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 0.26 \cdot C_{p,\text{m}}(\text{cr})\} \cdot \{\langle T \rangle - 298.15 \text{ K}\}. \tag{4}$$

The terms $C_{p,\text{m}}(\text{cr})$ and $C_{p,\text{m}}(\text{l})$ refer to the heat capacities of the solid and liquid phases, respectively, and were estimated according to a group additivity approach.[15] A liquid-phase group value Γ for the internal quaternary sp^2 carbon atom found in the internal carbons of coronene, corannulene, and perylene, is not available. Values of $\Gamma = 16$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} for the liquid and $\Gamma = 9.1$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} for the solid were used for these terms. The value of 9.1 J $\cdot$ K^{-1} $\cdot$ mol^{-1} replaces the tentative assignment of 4.44 J $\cdot$ K^{-1} $\cdot$ mol^{-1} reported previously,[15] and is based on the evaluation of additional data. The value of $\Gamma = 16$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} was estimated from $\Gamma(\text{l})/\Gamma(\text{cr})$ observed for quaternary aromatic carbon atoms and the 9.1 J $\cdot$ K^{-1} $\cdot$ mol^{-1} value evaluated for $\Gamma(\text{cr})$ of

TABLE 2. Gas-chromatographic retention times t_r

	Mixture 1				
T/K:	503.0	513.0	523.0	533.1	543.1
	t_r/s				
Carbon tetrachloride	139.5	141.1	143.3	144.5	146.1
Octadecane	227.8	208.7	196	185.9	179.5
Eicosane	309.9	267.8	239.2	218	203.8
Docosane	464.5	375.5	315.8	273.3	244.5
Tetracosane	753.5	571	450.8	368.2	312.5
Hexacosane	1290.5	923.4	687.4	529.8	425.5
Corannulene	1566.6	1171.2	900.2	708.7	574.2
Octacosane	2281	1553.8	1099.4	804.4	612.7
	Mixture 2				
T/K:	493.1	503.1	513.1	523.2	533.3
	t_r/s				
Carbon tetrachloride	136.7	138.4	140.4	142.1	143.4
Phenanthrene	282.7	252.1	230.4	214.7	202.1
Eicosane	369.2	307.6	266	237.3	216.4
Docosane	594.1	461.2	372.8	313.1	271.1
Tetracosane	1027.2	747.5	566.3	446.6	364.8
Corannulene	2137.6	1554.9	1160.3	891.3	701.7
	Mixture 3				
T/K:	523.2	533.2	543.2	553.2	563.2
	t_r/s				
Carbon tetrachloride	141.3	143	144.8	146.3	147.8
Docosane	312.3	270.7	241.3	220.8	206.2
Hexacosane	679.1	523.5	418.8	347.7	298.2
Octacosane	1085.5	793.9	602	468.9	387.2
Corannulene	889.1	699.9	565.1	474.3	398.5
	Mixture 4				
T/K:	543.2	553.2	563.2	573.2	583.2
	t_r/s				
Carbon tetrachloride	46.5	47.6	48.4	48.2	48.5
Octadecane	67.6	65	62.7	60	58.4
Eicosane	82.2	76.3	71.6	66.9	63.9
Docosane	105.9	94.4	85.5	77.5	72.1

TABLE 2—*continued*

Hexacosane	144.4	123.1	107	93.5	84.4
Corannulene	245.8	204.9	173.3	146.7	129.4
Octacosane	306.9	239.5	191.3	154.5	129.4
Perylene	348.9	283	232.9	192	162.9
Coronene	1313	984.5	748.7	572.1	448.9
T/K:	543.3	553.5	563.7	573.4	583.3

Mixture 5

	t_r/s				
Methylene chloride	39.1	39.8	39.7	39.9	39.7
Octadecane	58.1	54.8	52	49.8	48.4
Eicosane	70.7	64.4	59.4	55.5	53
Docosane	91.1	79.6	70.9	64.2	59.9
Tetracosane	124.5	103.8	88.7	77.4	70.2
Hexacosane	178.3	142	116.4	97.6	85.5
Corannulene	211.6	172.7	143.6	121	106.4
Octacosane	265.1	202.3	159	128.1	108.3
Perylene	301	239.1	193.4	158.7	96.2
Coronene	1129.9	829.1	622.3	475.3	377.7

the solid. This assumes a constant ratio for the two types of quaternary aromatic carbon atoms. The values used for each group and the total estimated heat capacity for each compound are summarized in table 5.

The sublimation enthalpy of corannulene adjusted to $T = 298.15$ K on the basis of equation (2) as measured by head space analysis is listed as the first entry in table 6. The second entry is the value for corannulene obtained by adding the vaporization enthalpy at $T = 298.15$ K to the fusion enthalpy adjusted similarly for temperature. The sublimation enthalpies calculated for coronene, perylene, and several of the standards used are listed in the last column of this table. The results obtained for coronene require some comment. Adjusting the value of the fusion enthalpy of coronene from $T = 710.5$ K to $T = 298.15$ K results in a negative fusion enthalpy. This adjustment is clearly unrealistic and is probably a consequence of using equation (4) over a temperature range that greatly exceeds its valid limits. [12–14] Equation (4) has been tested to about $T = 500$ K and found to give reasonable temperature adjustments. The melting temperature for coronene is simply beyond the applicable temperature range.

The sublimation enthalpies obtained in this study are compared with literature values in table 7. The results obtained for octadecane, eicosane, and phenanthrene are in very good agreement with those measured by other techniques. Octadecane and eicosane both melt at temperatures close to room temperature, and the temperature adjustment of the fusion enthalpy to room temperature is small. The temperature adjustment for phenanthrene,

TABLE 3. Molar enthalpies of transfer from solution $\Delta_{sln}^g H_m(\langle T\rangle)$ and enthalpies of vaporization $\Delta_l^g H_m$ (298.15 K) obtained by g.c. The n-alkanes and phenanthrene were treated as standards and the remainder as unknowns. The uncertainites were generated from the uncertainty associated with the slope of each correlation equation ($\pm\sigma$)

Expt. No.	1	2	3	4	5	1	2	3	4	5
$\langle T/\text{K}\rangle$:	523	513	543	543	563					
	$\Delta_{sln}^g H_m(\langle T\rangle)$ / kJ·mol^{-1}					$\Delta_l^g H_m$(298.15 K) / kJ·mol^{-1}				
Octadecane	54.7			50.2	51	90.7 ± 2.1			90.7 ± 2.8	90.5 ± 2.3
Eicosane	60.8	62.3		55.6	56.4	102.6 ± 2.1	102.5 ± 3.8		102.7 ± 3.1	102.5 ± 2.6
Docosane	67.0	68.5	64.2	61.0	62.0	114.8 ± 2.7	114.4 ± 3.9	115.4 ± 4.4	114.8 ± 3.4	115.1 ± 2.8
Tetracosane	73.1	74.8		66.4	67.4	127 ± 2.9	126.2 ± 4.2		126.8 ± 3.7	127.1 ± 3.0
Hexacosane	79.2		75.9		72.7	139 ± 3.2		139.8 ± 5.2		139 ± 3.3
Octacosane	85.2		81.3	77.2	77.9	150.8 ± 3.4		150.9 ± 5.5	150.8 ± 4.3	150.6 ± 3.6
Phenanthrene		49.0					77.3 ± 2.8			
Corannulene	67.7	68.8	65.9	59.5	62.6	116.2 ± 2.7	114.8 ± 3.8	118.9 ± 4.5	111.4 ± 3.3	116.3 ± 2.9
Perylene				64.4	65.9				122.4 ± 3.6	123.7 ± 3.0
Coronene				76.0	76.6				148.2 ± 4.2	147.7 ± 3.5

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TABLE 4. A comparison of reproducibility of the vaporization enthalpies $\Delta_l^g H_m$ (298.15 K) of the standards obtained in this study. The uncertainties represent two standard deviations of the mean value reported in table 3

Compound	$\dfrac{\Delta_l^g H_m (298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	
	Literature [9–11]	This work
Octadecane	91.4	90.6 ± 0.13
Eicosane	101.8	102.6 ± 0.14
Docosane	115.6	114.9 ± 0.33
Tetracosane	125.6	126.8 ± 0.4
Hexacosane	139.1	139.3 ± 0.5
Octacosane	151.4	150.8 ± 0.12
Phenanthrene	77.3	77.3
Corannulene		115.5 ± 2.5
Perylene		123.1 ± 1.7
Coronene		148.0 ± 0.5

TABLE 5. Group values Γ used in estimating the molar heat capacities $C_{p,m}$ of the liquid and solid compounds of this study

Group	$\dfrac{\Gamma(l)}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\dfrac{\Gamma(cr)}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
Primary sp^3 CH$_3$ (A)	34.9	36.6
Secondary sp^3 CH$_2$ (B)	31.9	26.9
Tertiary sp^3 CH (C)	22.4	9.0
Tertiary aromatic sp^2 CH (D)	21.8	17.5
Quaternary aromatic sp^2 C (E)	15.3	8.5
Internal quaternary aromatic sp^2 C (F)	16	9.1

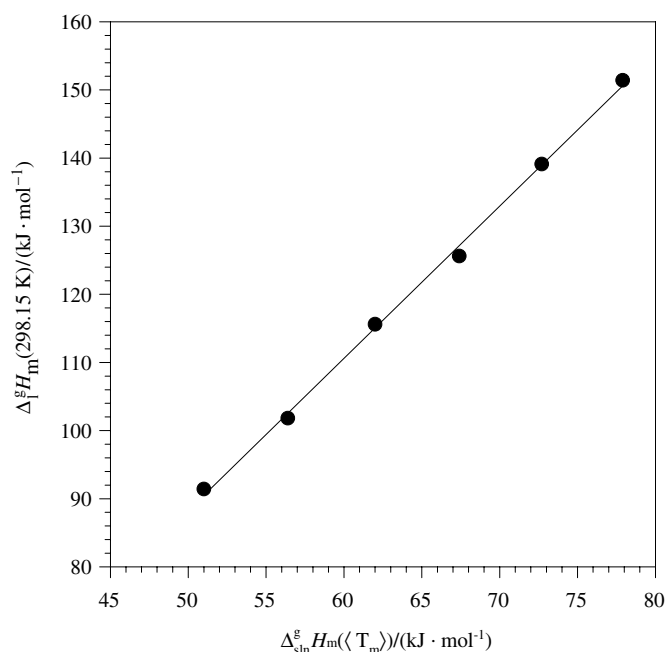|	Group sum	$\dfrac{C_{p,m}(l)}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\dfrac{C_{p,m}(cr)}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
Octadecane	$2 \cdot A + 16 \cdot B$	580	510
Eicosane	$2 \cdot A + 18 \cdot B$	644	563
Docosane	$2 \cdot A + 20 \cdot B$	676	617
Phenanthrene	$10 \cdot D + 4 \cdot E$	279	209
Corannulene	$10 \cdot D + 5 \cdot E + 5 \cdot F$	374.5	263.0
Perylene	$12 \cdot D + 6 \cdot E + 2 \cdot F$	385.4	279.1
Coronene	$12 \cdot D + 6 \cdot E + 6 \cdot F$	449.4	315.5

FIGURE 2. The correlation of vaporization enthalpy $\Delta_l^g H_m$ (298.15 K) against the enthalpy of transfer from solution to the vapor $\Delta_{sln}^g H_m(\langle T/K \rangle)$ for run 5 of table 3. The equation of the straight line is given by: $\Delta_l^g H_m$ (298.15 K) = $(2.23 \pm 0.05) \cdot \Delta_{sln}^g H_m(\langle T \rangle) - (23.3 \pm 1.0)$ kJ $\cdot$ mol^{-1} with correlation coefficient $r^2 = 0.9981$.

TABLE 6. Values of the enthalpies of sublimation $\Delta_{cr}^g H_m$ (298.15 K), vaporization $\Delta_l^g H_m$ (298.15 K), and fusion $\Delta_{cr}^l H_m(T_{fus})$, and melting temperatures T_{fus} used in calculating sublimation enthalpies at $T = 298.15$ K

Compound	$\dfrac{\Delta_l^g H_m(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\dfrac{\Delta_{cr}^l H_m(T_{fus})}{\text{kJ} \cdot \text{mol}^{-1}}$	T_{fus}/K	$\dfrac{\Delta_{cr}^l H_m(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\dfrac{\Delta_{cr}^g H_m(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$
Corannulene					119.5 ± 4.4^a
Corannulene	115.5 ± 2.5	17.3 ± 1.2	542.3	0.5 ± 5.5	116.3 ± 6.0^b
Perylene	123.1 ± 1.7	$31.9^{(31)}$	551.3	14.6 ± 5.7	137.7 ± 5.9
Coronene	148 ± 0.5	$19.2^{(31)}$	710.5	-13.5	>148
Octadecane	90.6 ± 0.1	$61.5^{(31)}$	301.3	61.2	151.9
Eicosane	102.6 ± 0.2	$69.0^{(36)}$	309.6	67.9	169.3
Docosane	114.9 ± 0.8	$78.5^{(36)}$	316.9	76.8	190.5
Phenanthrene	77.3	$16.7^{(36)}$	347.5	13.9	91.2

^{a} Head space analysis; ^{b} correlation-gas chromatography, fusion enthalpy.

TABLE 7.   A comparison of molar enthalpies of sublimation $\Delta_{cr}^{g}H_m$ (298.15 K) with literature values

Compound	$\Delta_{cr}^{g}H_m$(298.15 K)	
	kJ · mol^{-1}	kJ · mol^{-1}
	(This work)	(Literature)^a
Octadecane	151.9 ± 0.3	152.7 ± 1.6[17] 153.1[18]
Eicosane	169.3 ± 0.7	170.4[17]
Phenanthrene	91.2	91.3 ± 2.7[11]
Perylene	138.1 ± 6.2	137.2 ± 5.9[19] 126.8[20] 145.4 ± 2.5[21]
		144.1[22] 134.6 ± 5.4[23]
Coronene	>144	141 ± 10.5[19] 143.2[20] 138.9[25]
		155.3[22] 154.7[23] 144.1 ± 6.9[24]
Corannulene	118.3 ± 3.3	

^{a} Sublimation enthalpies were adjusted to $T = 298.15$ K with equation (2).

$T_{fus} = 347$ K, is larger. The sublimation enthalpies calculated using equation (4) are in good agreement with the literature values.

The values obtained for the sublimation enthalpy of corannulene by head space analysis and correlation-gas chromatography-d.s.c. are in good agreement. A weighted mean value of (118.3 ± 3.3) kJ · mol^{-1} is calculated on the basis of a weighting factor inversely proportional to the uncertainties associated with each measurement. The uncertainty represents two standard deviations of the mean. The value of 121.4 kJ · mol^{-1} estimated from an empirical non-bonded atom–atom potential proposed by Williams[16] on the basis of the crystal structure is in good agreement with these experimental results.[16]

The sublimation enthalpy of (138.1 ± 6.2) kJ · mol^{-1} obtained in this work for perylene is in very good agreement with the most recent value reported, but at variance with several others; it is in reasonable agreement with the mean of all the values, (135.9 ± 6.8) kJ · mol^{-1}. The average of (137.2, 134.6, and 138.1) kJ · mol^{-1}, namely, (136.6 ± 2.1) kJ · mol^{-1}, is recommended for the sublimation enthalpy of perylene.

Taking into account the uncertainty associated with the vaporization enthalpy of coronene, (148 ± 4) kJ · mol^{-1}, the sublimation enthalpy must be several kJ · mol^{-1} larger than 144 kJ · mol^{-1}. Two values consistent with this assumption and both in good agreement with each other, have been reported. The mean of (155.3 and 154.7) kJ · mol^{-1}, 155 kJ · mol^{-1}, is recommended for the value of coronene. The uncertainty associated with this sublimation enthalpy is difficult to assess. The magnitude of the sublimation enthalpy should probably exceed 148 kJ · mol^{-1} but must be less than 176.2 kJ · mol^{-1}(148 kJ · mol^{-1} + 28.2 kJ · mol^{-1}, table 6). An uncertainty of ±7.0 kJ · mol^{-1} (two standard deviations) has been arbitrarily assigned.

A comparison of the gas-phase enthalpies of formation of corannulene, perylene, and coronene with those calculated by various theoretical and empirical methods is given in

TABLE 8. A comparison of experimental and theoretical enthalpies of formation $\Delta_f H_m$ (298.15 K)

	Corannulene	Perylene	Coronene
Experimental			
$\Delta_f H_m$(cr)/(kJ $\cdot$ mol^{-1})	342.3 $\pm$ 5.6 [4]	182.8 $\pm$ 0.8 [26]	152.5 $\pm$ 6.9 [27, 35]
$\Delta_{cr}^{g} H_m$/(kJ $\cdot$ mol^{-1})	118.3 $\pm$ 3.3	136.6 $\pm$ 2.1	155 $\pm$ 7.0
$\Delta_f H_m$(g)/(kJ $\cdot$ mol^{-1})	460.6 $\pm$ 6.5	319.4 $\pm$ 2.2	307.5 $\pm$ 9.8
		$\Delta_f H_m$(g, 298.15 K) kJ $\cdot$ mol^{-1}	
Theoretical method			
HF/STO-3G [28]a	516.3	305.9	256.1
HF/3-21G [28]a	504.2	310	259.4
HF/6-31G* [28]a	490.4	310.5	258.2
HF/6-31G* [29]a		332.9	
HF/6-31G* [30]a			290.4
HF/TZpp [30]a			292.0
HF/6-311G** [30]a			293.3
B3LYP/6-31G* [30]a			300.8
B3LYP/6-311G** [30]a			300.4
MP2/6-31G* [30]a			274.1
Group additivity(1) [32]	460	280	323
Group additivity(2) [33]		331.8	336.4
AM1	655 [33]	373.6 [4]	402.6b
MNDO	561.8 [4]	352.4b	347.5b
PM3	584.5 [34]	343.2b	366.1

a Lack of agreement on how to extract enthalpies of formation from computed total energies accounts for the discrepancies observed in $\Delta_f H_m$ (g, 298.15 K) values reported for the same compound calculated at the same level of theory; *b* this work.

table 8. The results for corannulene are very similar to those previously published on the basis of an estimated sublimation enthalpy. Of the three comparisons, the calculated values for corannulene seem in poorest agreement, while the theoretical results obtained for coronene and perylene are in better agreement. As a general observation, *ab initio* methods with large scale basis sets seem to provide the better results.

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