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Heat capacities of liquid polycyclic aromatic hydrocarbons

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Abstract

Liquid heat capacities of 14 aromatic hydrocarbons were measured using a DSC calorimeter. Measurements were performed in the temperature range 100 K above the melting temperature of each hydrocarbon. The lowest and highest temperatures considered were respectively 303 and 692 K. Experimental results were correlated using Benson's group contribution approach. The group parameters determined allow the experimental results to be represented to within 2%.

Keywords: Fused-ring aromatics; Group contributions; Heat capacity

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List of symbols

C_p^0, C_p^1	parameters for liquid heat capacity representation (Eq. (1))
C_p	heat capacity/(J mol^{-1} K^{-1})
H	hydrogen atom
Cb	carbon atom in the aromatic ring
Cbf	carbon atom in the fused aromatic ring
a, b	parameters for group contribution values
T	temperature/K
$T_{\min}$, $T_{\max}$	start and end of the temperature range/K

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1. Introduction

The heat capacities of liquid fused-ring aromatic hydrocarbons are not well known and only few experimental data can be found in the literature. McCullough et al. [1] measured the heat capacities of naphthalene and Finke et al. [2] determined the heat capacities of methylnaphthalenes, phenanthrene, fluorene and acenaphtene. No experimental data exist for more complicated aromatic structures. The objective of the present work was to complete the existing data and to extend the validity of the predictive method towards heavy aromatics. The heat capacities of 14 compounds containing up to 8 aromatic rings were measured as a function of temperature.

2. Experimental

The compounds studied together with the corresponding purities (as given by the manufacturers) are listed in Table 1. The purity of pentacene was unknown and its analysis by classical methods was not possible.

As in our previous study [3], heat capacities were determined using a Setaram DSC 111 differential scanning calorimeter. The apparatus was calibrated with alumina using a temperature jump of 2 K. The sensibility polynomial was determined for two temperature ranges: the first between 293 and 573 K, and the second between 543 and 803 K.

In Table 2, results obtained with benzene, naphthalene and phenanthrene are compared with data published in the literature. In the case of benzene, the data compiled and recommended by Goodwin [4] were used. Mean deviations observed are between 1.3% with benzene and 1.9% with phenanthrene. Therefore, a global accuracy of the present measurements is better than 2%.

3. Experimental results

Heat capacities were measured in the temperature range 100 K above the melting temperature of the compound considered. In the case of benzene, measurements were carried out between 303 and 347 K (an interval of 40 K). Temperature ranges corresponding to the particular compounds are listed in Table 3. Measurements cover a wide temperature interval between 303 and 692 K. A linear dependence of the heat capacities as a function of temperature was observed with all the aromatic hydrocarbons studied. Therefore, experimental results (50 determinations for a given compound) were deduced using the equation

$$C_p = C_p^0 + C_p^1 T \tag{1}$$

and the resulting parameters C_p^0 and C_p^1, together with the corresponding temperature ranges are listed in Table 3. The correlation coefficient was equal to 1 for all the heat capacity data series. For this reason, rough experimental data are not given here.

Table 1
List of compounds studied with their formula, origin and purity

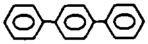
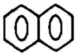
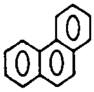
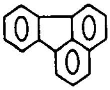
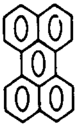
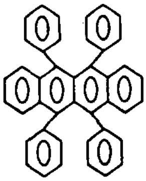
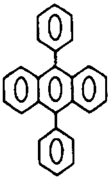
Compound	Formula	Source	Purity (%)
Benezene		Aldrich	99.99
Biphenyl		Aldrich	99
p-Terphenyl		Aldrich	99+
P-Quaterphenyl		Aldrich	99.5
Naphthalene		Prolabo	99
Anthracene		Aldrich	99.9
Naphtacene		Aldrich	99
Pentacene		Aldrich	-
Phenanthrene		Aldrich	>98
Fluoranthene		Aldrich	98
Pyrene		Aldrich	>99
Perylene		Aldrich	99+
Rubrene		Aldrich	98
9,10-Diphenylanthracene		Aldrich	99

Table 2
Comparison of the present results with literature data

Compound	Ref.	Temperature in K	C_p J mol^{-1} K^{-1}	C_p (this work) J mol^{-1} K^{-1}	Deviation %
Benezene	[4]	300	138.86	136.54	1.7
		310	141.15	138.84	1.6
		320	143.44	141.28	1.5
		330	145.72	143.84	1.3
		340	148.01	146.51	1.0
		350	150.29	149.28	0.7
					1.3
Naphthalene	[1]	360	223.822	219.827	1.8
		370	227.374	223.677	1.6
					1.7
Phenanthrene	[2]	383.27	314.085	305.21	2.8
		390.14	316.168	309.03	2.2
		398.70	318.764	313.68	1.6
		408.64	321.780	318.65	0.9
					1.9
			Global mean deviation (%)		1.6

Table 3
Experimental results

Compound	C_p^0	C_p^1	T_{min}–T_{max} in K
Benezene	70.28	0.2286	303–347
Biphenyl	188.29	0.2503	373–473
p-Terphenyl	149.35	0.6135	492–592
p-Quaterphenyl	425.22	0.4591	600–674
Naphthalene	95.95	0.3552	373–473
Anthracene	113.21	0.4970	492–592
Naphtacene	292.24	0.3498	634–690
Pentacene	87.69	0.8464	546–594
Phenanthrene	197.84	0.3033	392–492
Fluoranthene	131.46	0.4953	492–592
Pyrene	105.52	0.5881	492–592
Perylene	150.53	0.6303	552–652
Rubrene	412.01	1.2314	592–692
9,10-Diphenylanthracene	140.09	0.9934	522–62

4. Group contribution approach

Following Benson's concept, the heat capacities of the compounds studied in this work can be represented using 5 groups: Cb–$(Cb)_2(H)$, Cb–$(Cb)_3$, Cbf–$(Cb)_2(Cbf)$, Cbf–$(Cbf)_2(Cb)$ and Cbf–$(Cbf)_3$.

The first can be determined using the heat capacities of benzene in the temperature interval 303–347 K and is given by the equation

$$C_p(\text{Cb–(Cb)}_2\text{(H)}) = 0.0381\,T + 11.7 \tag{2}$$

In Fig. 1, the contribution of the group Cb–$(\text{Cb})_2$(H) given by Eq. (2) is compared with the third-degree polynomial proposed by Luria and Benson [5]. As can be observed, both relationships give very similar results above 300 K. The contribution of the Cb–$(\text{Cb})_2$(H) group established in this way was used in all further calculations. Therefore, Eq. (2) was extrapolated up to 692 K in some cases.

The second group corresponds to an aromatic carbon substituted with a phenyl group. This contribution was found using experimental data for biphenyl, *p*-terphenyl and *p*-quaterphenyl. In Fig. 2, the heat capacities of these compounds at 500 K are plotted as a function of the number of aromatic rings. The slope of the straight line is given by $[4\text{Cb–(Cb)}_2\text{(H)} + 2\text{Cb–(Cb)}_3]$. Therefore, the contribution of Cb–$(\text{Cb})_3$ at 500 K can be established. Repeating this calculation for various temperatures, it was observed that its value was constant to within the experimental accuracy of the present measurements and equal to 6 J (groupmol) K^{-1}. Thus

$$C_p[\text{Cb–(Cb)}_3] = 6\ \text{J (groupmol)}^{-1}\ \text{K}^{-1} \tag{3}$$

was retained in subsequent calculations.

A similar analysis was applied to the series of fused ring aromatics: naphthalene, anthracene, naphtacene and pentacene. As an example, the plot of the heat capacities of these compounds at 500 K is given in Fig. 3. In this case, the slope of the straight line is

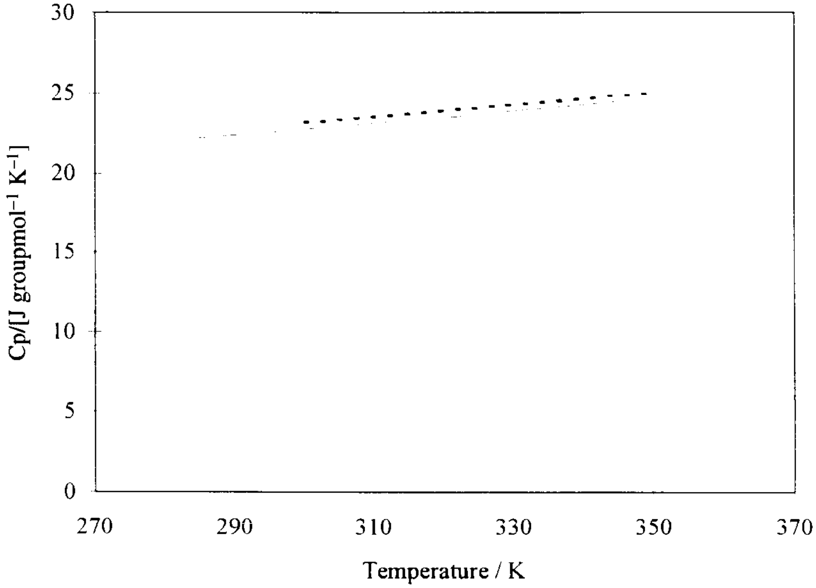


Fig. 1. Contribution of the group Cb–$(\text{Cb})_2$(H) as a function of temperature according to the present work (– – –) and to Luria and Benson (—).

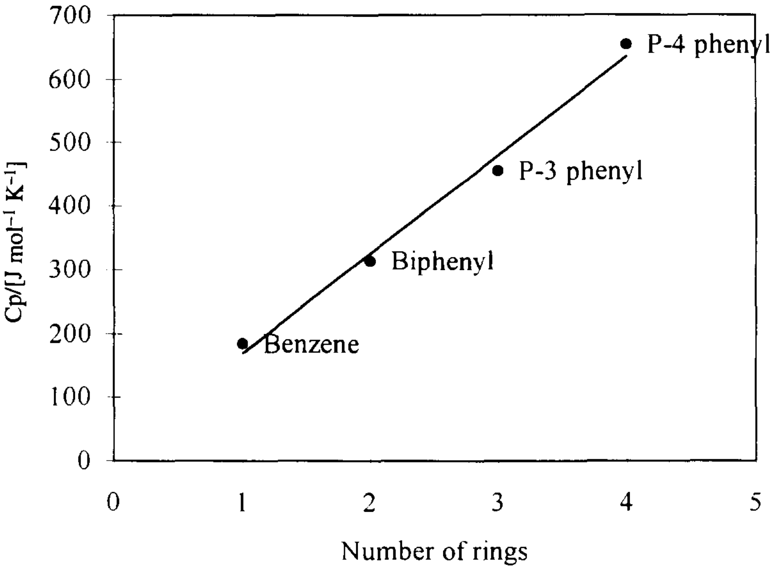


Fig. 2. Heat capacity of benzene, biphenyl, *p*-terphenyl and *p*-quaterphenyl versus the number of rings, at $T = 500$ K.

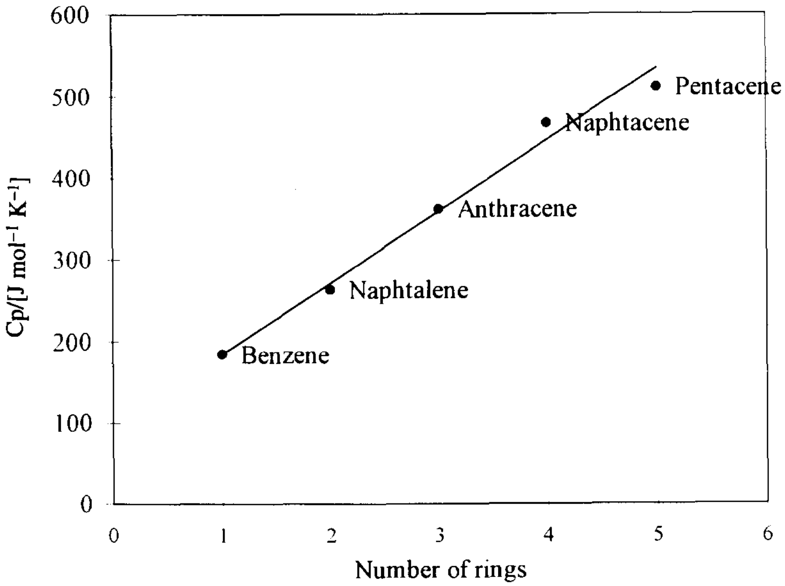


Fig. 3. Heat capacity of benezene, naphthalene, anthracene, naphtacene and pentacene versus the number of rings, at $T = 500$ K.

given by [2Cb–$(Cb)_2(H)$ + 2 Cbf–$(Cb)_2(Cbf)$] and the corresponding value of the Cbf–$(Cb)_2(Cbf)$ group could be determined. As previously, calculations performed at various temperatures demonstrated that this contribution was temperature-invariant and equal to

$$C_p[\mathrm{Cbf{-}(Cb)_2(Cbf)}] = 13\ \mathrm{J\ (groupmol)^{-1}\ K^{-1}} \tag{4}$$

The Cbf–$(Cbf)_2(Cb)$ and Cbf–$(Cbf)_3$ groups can be found in phenanthrene, fluoranthene, and perylene, and in fluoranthene, pyrene, and perylene, respectively. At first, it was assumed that both these groups are equivalent to the Cbf–$(Cb)_2(Cbf)$ group. Calculation results showed that this assumption was reasonable and that the accuracy of the present data did not allow any further refinement of the group contribution values. The list of the group contributions established in this study is given in Table 4.

Table 4
Group contribution values: C_p (group) = $aT + b$

Group	a	b
Cb–$(Cb)_2(H)$	0.0381	11.7
Cb–$(Cb)_3$	0	6
Cbf–$(Cb)_2(Cbf)$	0	13
Cbf–$(Cbf)_2(Cb)$	0	13
Cbf–$(Cbf)_3$	0	13

Table 5
Comparison between experimental (Eq. (1)) heat capacities and those calculated by Benson's method (Eqs. (2)–(4))

Compound	Mean deviation (%)
Benezene	0.00
Biphenyl	1.50
p-Terphenyl	0.90
p-Quaterphenyl	4.70
Naphthalene	1.02
Anthracene	1.78
Naphtacene	0.50
Pentacene	0.70
Phenanthrene	1.68
Fluoranthene	0.80
Pyrene	5.30
Perylene	1.90
Rubrene	3.11
9,10-Diphenylanthracene	3.08
Global mean deviation (%)	2.1

In Table 5, mean deviations between experimental data and group contribution estimates are given for all the compounds studied. The global mean deviation was about 2.1% which corresponds to the experimental accuracy of the present data.

5. Conclusion

The experimental study of 14 polycyclic aromatics demonstrated that the heat capacities of these compounds change linearly with temperature.

An analysis of the experimental results confirmed the applicability of Benson's method to this class of compounds. It is interesting to note that only three group contributions were necessary and that two of them were temperature-independent. Therefore, to represent heat capacities of liquid heavy aromatics to within 2%, only four parameters are needed.

References

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