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DIFFERENTIAL CALORIMETRIC STUDY OF POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

The temperature, enthalpy, entropy of melting and crystal transitions of 21 polycyclic aromatic hydrocarbons, containing from 2 to 6 unsubstituted condensed rings, were determined by differential scanning calorimetry. The temperature and the molar entropy of melting generally increase with increasing degree of symmetry and molecular size of the hydrocarbon. Apparent deviations from this trend are discussed in terms of molecular distorsion due to steric interaction between neighbouring hydrogens.

INTRODUCTION

Polycyclic aromatic hydrocarbons belong to an extensively studied class of compounds. Besides their broad scientific interest, they have practical significance in biology and medicine, in the field of combustion and pollution, in the technology of coal tar and of carbon black.

This paper refers on the determination, by differential scanning calorimetry (DSC), of the temperature, enthalphy, and entropy of fusion, as well as of crystal transitions, of 21 polycyclic aromatic hydrocarbons containing from 2 to 6 unsubstituted condensed rings.

Several authors have studied these compounds from widely different standpoints. However, the basic thermodynamic data available from the literature refer only to the simplest compounds. Furthermore, apart from a limited number of data obtained by conventional calorimetry, the relevant values were obtained almost exclusively by indirect techniques. It was hoped that our DSC measurements on a representative series of hydrocarbons should allow us to ascertain whether the thermodynamic data correlate with some structural parameters of the hydrocarbons.

From a formal point of view, the polycyclic hydrocarbons can be considered as belonging to an homologous series. In principle, it is then conceivable that a correlation exists between their thermodynamic properties and structural parameters such as molecular size and molecular symmetry. Correlations of this kind are well known for the n-paraffin series.

The relationship between structures and melting temperatures of a series of polycyclic aromatic hydrocarbons was discussed since 1947 by Kravchenko[1]. It was observed that in the linear series (naphthalene to naphthacene) and in the linear-angular series (phenanthrene, benzo- and dibenzophenanthrenes) the difference Δt between the melting points of neighboring members is much larger than for the "circular" series (phenanthrene to coronene). The similar melting temperatures of "condensation isomers", such as 1,2:7,8-dibenzoanthracene, 1,2:5,6-dibenzoanthracene, 1,2-benzonaphtacene and 1,2:3,4:7,8-tribenzoanthracene, 1,2:3,4-dibenzopyrene were attributed to the common presence of the same skeleton, *i.e.* that of 1,2-benzoanthracene and triphenylene respectively.

Pospelov and Grigor'ev[2] have worked out mathematical expressions that correlate the melting temperatures of a limited number of polycyclic hydrocarbons to their molecular weight, the number of possible axes of rotation and the coefficient of "mechanical strength" of the molecules. The above expressions are different for different series (linear, angular and linear-angular).

EXPERIMENTAL

Materials and apparatus

Anthracene, phenanthrene, pyrene, chrysene, 3,4-benzopyrene, 1,2:5,6-dibenzoanthracene "puriss."; naphthalene, acenaphthene, fluoranthene, perylene, 1,12-benzoperylene, 1,2-benzoanthracene "purum" (Fluka AG, Buchs, Switzerland); 1,2:3,4-, 1,2:4,5-, 3,4:9,10-dibenzopyrene "puriss." (Koch-Light Lab. Ltd., Colnbrook, England); pycene 95–96%, 3,4-benzophenanthrene, triphenylene, 1,2-benzopyrene (Schuchard, München, Germany); 1,2:3,4-dibenzoanthracene (Natl. Biochemicals Corp., Cleveland, Ohio, USA).

The IR and UV-visible spectra of the above samples correspond to those reported in the API cards. All the substances whose calorimetric curve showed a "pre-melting" (viz. a melting peak whose ascending side did not rise sharply above the base line) were purified by complexing with pyromellitic dianhydride[3]. This was

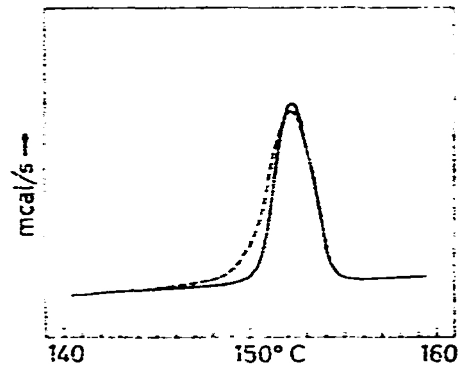

Fig. 1. – – –, DSC curve of "pure grade" pyrene; ———, DSC curve of pyrene, purified by complexing with pyromellitic dianhydride. Heating rate 8 °C/min.

done for the following compounds: chrysene, acenaphthene, phenanthrene, pyrene, 1,2-benzoanthracene, 1,2:3,4-dibenzoanthracene. As an example, DSC curves of pyrene are given in Fig. 1. The purity of the hydrocarbons recovered from the complexes was checked by UV–visible spectroscopy and by DSC.

For this work we used a differential scanning calorimeter Perkin–Elmer Model 1B. The enclosure surrounding the sealed pan was kept under a dynamic nitrogen atmosphere throughout the experiments. The operating conditions were the same reported for previous work on molecular complexes of polycyclic aromatic hydrocarbons[4,5].

Operating procedure

From 3 to 5 mg of the sample, placed in sealed aluminium pans for volatile materials, were run at 16 °C/min between 30–35 °C and the temperature of complete melting. The melted sample was cooled and maintained at room temperature for about one hour, to allow complete recrystallization, and then submitted to repeated heating–cooling cycles in the calorimeter.

Although the non-uniformity of the sample does not affect the precision of the determination of ΔH, it noticeably affects the peak shapes; therefore, the calorimetric curves related to the first melting of the same sample are generally not superimposable. For this reason the data considered in the present work refer to runs from the second to the following runs (unless specifically mentioned).

Due to the high thermal stability of the investigated hydrocarbons, such repeated runs were reproducible within the accuracy limits of the instrument.

The enthalpy of fusion for the examined compounds was calculated relative to that of a weighed indium sample, of purity above 99.999% ($\Delta H = -6.79$ kcal/g). Temperature calibrations were carried out using two standards: indium (m.p. 156 °C), and lead (m.p. 327 °C), the latter for the hydrocarbons melting above 290 °C. The characteristic temperatures were determined by tracing a segment, with a slope equal to that of the ascending side of the melting peak of the standard, from the maximum to the peak base line. This is shown in Fig. 2 for chrysene, anthracene and triphenylene. The temperature was read at the point where the edge of the standard peak and the sample base line intersect.

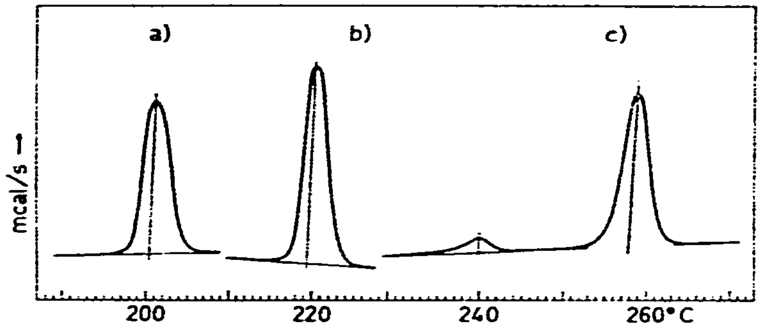

Fig. 2. DSC curves of triphenylene (a), anthracene (b), and chrysene (c).

The areas limited by the melting curves and the base line were measured by a planimeter.

RESULTS

The values of temperatures, enthalpies, and entropies of melting of the polycyclic hydrocarbons are reported in Table 1. For each hydrocarbon at least five runs with different weighed samples were made. The data represent the average of these values. The standard deviations were calculated on the mean values. In the same table ΔH and ΔS data available in the literature are also given.

TABLE 1

TEMPERATURES, ENTHALPIES, AND ENTROPIES OF MELTING

Hydrocarbon	*m.p. (°C)*	ΔH_f *(kcal mole*$^{-1}$*)*		ΔS_f *(cal mole*$^{-1}$ K^{-1}*)*	
		This work	*Reference*	*This work*	*Reference*
Naphthalene	79 ±0.8	4.57±0.12	4.56[b] 4.59[c] 4.50[d]	12.98±0.35	12.8[l]
Acenaphthene	89.9±0.1	5.21±0.09	5.23[e] 4.95[f] 4.87[g]	14.34±0.25	13.3[m]
Fluorene	112.4±0.3	4.48±0.08	4.67[e]	11.60±0.22	
Anthracene	219.5±0.2	6.89±0.27	6.93[e] 6.90[b,h]	13.99±0.55	14.4[n]
Phenanthrene	98.1±0.5	4.00±0.07	3.89[e] 4.33[b] 4.45[h]	10.78±0.20	12.1[o]
Fluoranthene	107.8±0.2	4.51±0.07	4.48[i]	11.84±0.18	11.7[l]
Pyrene	151.3±0.1	4.09±0.09	4.15[i]	9.64±0.21	9.8[l]
3,4-Benzophenanthrene	61.6±0.8	3.90±0.17		11.65±0.52	
1,2-Benzoanthracene	161.1±0.4	5.11±0.03		11.76±0.06	
Chrysene	258.2±0.4	6.25±0.02		11.76±0.04	14.9[p]
Triphenylene	200.4±0.4	6.00±0.11	5.91[i]	12.65±0.2	12.6[l]
Perylene	280.7±0.3	7.59±0.14		13.70±0.24	13.8[l]
1,2-Benzopyrene	181.3±0.1	3.96±0.08		8.72±0.18	
3,4-Benzopyrene	181 ±0.3	4.14±0.07		9.11±0.12	
Picene[a]	364 ±0.5	8.41±0.18		13.20±0.29	
1,2:5,6-Dibenzoanthracene	271 ±0.4	7.45±0.12		13.69±0.22	
1,2:3,4-Dibenzoanthracene	280.3±0.8	6.17±0.08		12.82±0.35	
1,12-Benzoperylene	281 ±0.4	4.15±0.11		7.48±0.19	
1,2:3,4-Dibenzopyrene	228 ±0.4	5.90±0.11		11.78±0.19	
3,4:9,10-Dibenzopyrene	283.6±0.1	6.66±0.14		11.96±0.26	
1,2:4,5-Dibenzopyrene	247 ±0.5	7.29±0.13		14.02±0.4	

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[a] No complex with PMDA. Repeated crystallization from different solvents did not improve purity. DSC runs performed with a 95–96% compound. [b] C. D. Hodgman (ed.), *Handbook of Chemistry and Physics*, Chemical Rubber Co., New York, 1962, 44th ed. [c] M. E. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, 36 (1932) 882. [d] H. L. Ward, *J. Phys. Chem.*, 38 (1934) 761. [e] Ref. 6. [f] E. L. Skau, *J. Phys. Chem.*, 39 (1935) 761. [g] H. W. Sadowska, G. B. Stepniewska and R. M. Recko, *Przem. Chem.*, 48 (1969) 282. [h] Ref. 9. [i] Ref. 7. [l] A. A. K. Al-Mahdi and A. R. Ubbelohde, *Proc. Roy. Soc. Ser.*, 220 (1953) 143. [m] E. W. Washburn, *International Critical Tables*, 4 (1928) 180. [n] C. A. Fyfe, Personal communication, June 1970, ref. 7. [o] P. Goursot and E. F. Westrum, *J. Chem. Eng. Data*, 13 (1968) 471. [p] Ref. 8.

The ΔH values obtained in the present work are in good agreement with those recently obtained by Wauchope and Getzen[6] using DSC, for acenaphthene, fluorene, anthracene and phenanthrene. The present ΔH and ΔS data are also in excellent agreement with those obtained by Wong and Westrum[7] by conventional calorimetry for pyrene, fluoranthene, and triphenylene.

Other data reported in Table 1 are from authors who determined by different techniques the enthalpies of melting of perylene and chrysene, besides those of the before mentioned compounds.

The present data are reasonably close to those reported in the literature, except for chrysene[8] and phenanthrene[9]. However, values not based on direct calorimetric determinations, as in the case of chrysene (whose entropy of melting was determined by crioscopy) might be less accurate than the calorimetric ones[7].

Pentacene, which was originally included in our work, did not show a well defined melting peak. Also the energy of melting of coronene could not be determined precisely; the uncertainty of our measurement is very probably due to the fact that this hydrocarbon melts close to the upper temperature limit of the instrument.

Table 2 gives the temperatures and enthalpies of transition for the hydrocarbons whose DSC curves show, before the fusion endotherm, a peak attributable to a crystal transition. The crystal transition of phenanthrene was previously observed by Matsumoto[10] and Matsumoto and Fukuda[11]. By X-ray diffraction studies at different temperatures the above authors ascertained that the transition consists of an increase of the lattice constants with increased temperature (higher order phase transitions), the crystal system and the space group remaining unchanged.

TABLE 2

TEMPERATURE RANGE AND ΔH OF CRYSTAL TRANSITIONS

Hydrocarbon	*T (°C)*	*ΔH (kcal mol^{-1})*
Chrysene	234—244	0.77 ± 0.05
Phenanthrene	58—71	0.3[b]
1,2-Benzopyrene[a]	147—159	0.6[b]
3,4-Benzopyrene[a]	110—123	2.03 ± 0.02

[a]Transition peak observed only when heating previously unmelted samples. [b]Curves too broad to allow a precise measurement.

Fig. 3 shows a plot of the melting temperatures against the number of carbon atoms (n_C). A similar plot of ΔH versus n_C does not show any apparent regularity. Fig. 4 shows a plot of $\Delta S/n_C$ versus n_C. As previously indicated by Wong and Westrum on the basis of data on ten hydrocarbons, the function decreases rapidly at first, and then smoothes out to an asymptotic value around 0.5–0.6 cal mol^{-1}K^{-1} (ref. 7).

DISCUSSION

The melting temperatures show the expected trend of increasing by increasing the number of carbon atoms. The dispersion of the data relative to the least square line of Fig. 3 appears to reflect the impact of molecular symmetry.

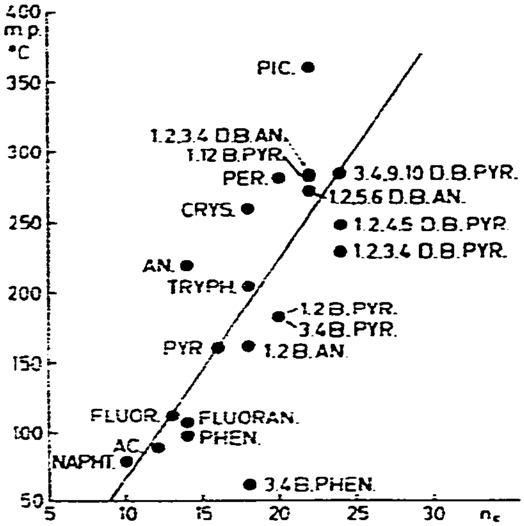
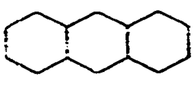


Fig. 3. Plot of melting temperatures (m.p.) of polycyclic hydrocarbons against number of carbon atoms (n_C).

Only a few polycyclic aromatic hydrocarbons are truly symmetric in the sense of possessing one or more elements of symmetry. The hydrocarbons of the linear series such as anthracene (A) possess three planes of symmetry (including the plane of the molecule) and therefore belong to the space group D_{2h}. Also the more compact molecule of pyrene has a D_{2h} symmetry.

Phenanthrene (B), though formally belonging to the C_{2v} point-group[12], should be probably considered as "pseudo-symmetric". In fact, because of the steric interaction between the "angular" hydrogens in position 4 and 5, the phenanthrene molecule is supposed to be slightly distorted, especially in the liquid state. Among the angularly condensed hydrocarbons, 3,4-benzopyrene was found to be non planar in the solid state[13]. Also the *peri*-condensed perylene is non planar[14,15]. The steric interaction between neighboring hydrogens is more severe when the hydrogens are in a more crowded situation[16]. This is the case of triphenylene[17] and, even more, of



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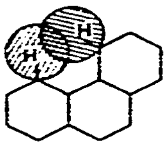

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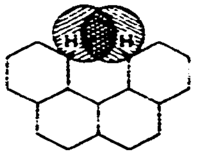

C

3,4-benzophenanthrene (C)[18]. It is therefore not surprising that anthracene (planar) falls above the curve of Fig. 3, while 3,4-benzophenanthrene (non planar) falls below the curve.

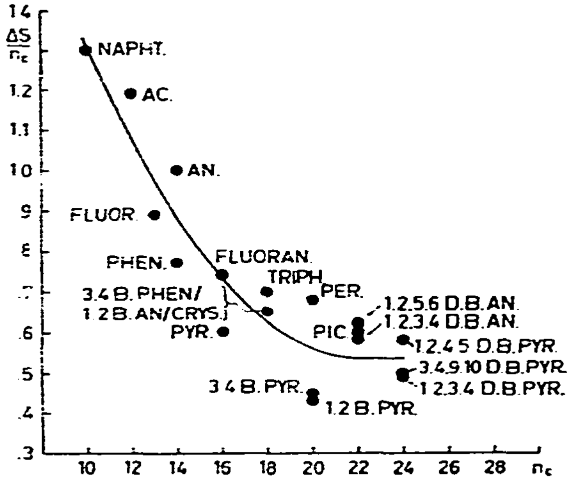

Fig. 4. Plot of molar entropy of fusion/number of carbon atoms ratio against number of carbon atoms of the hydrocarbon.

As shown in Fig. 4, molecular size and symmetry affect also the entropy of fusion of the polycyclic aromatic hydrocarbons, though in a more complex way than melting temperatures. It can be reasonably assumed that the rotation and vibration energies contribute substantially to the value of total fusion entropy in the crystal. It is also expected that the transition from the solid to the liquid state does not cause substantial energy changes in small and non symmetrical molecules, while large and highly symmetrical molecules, which are held rather rigidly in the crystalline lattice, acquire a larger vibrational freedom and a wider possibility of rotational reorientation[7].

If hydrocarbons belonging to the phenanthrene and to the pyrene series are considered separately, a trend seems apparent of increasing the ΔS value with increasing the molecular size and symmetry.

3,4-Benzopyrene and 1,2:5,6-dibenzoanthracene do not fit into the above scheme, as their ΔS is higher than suggested merely on account of size and symmetry considerations. It is conceivable that such a high ΔS value is associated to the above molecules being more planar in the crystal than in the liquid state, a feature that was already observed in the case of diphenyl[19,20]. Moreover, the different degree of freedom of the aromatic hydrocarbons in the crystal lattice and in the melt most likely depend also on factors such as the polarizability of the π-electron cloud, the bond distances and the charge densities at the carbon atoms.

ACKNOWLEDGEMENTS

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