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Heats of Sublimation of Polycyclic Aromatic Hydrocarbons and Their Molecular Packings

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The vapour pressure of some polycyclic aromatic hydrocarbons was measured by means of the effusion method. From the temperature dependence of the pressure, the heat of sublimation (ΔH kcal/mol) and the entropy ($\Delta S°$ cal/mol·deg) were calculated for the following hydrocarbons: 1, 2-benzanthracene ($\Delta H=28.8$; $\Delta S°=44._8$), tetracene (29.8; $43._3$), chrysene (28.1; $43._0$), triphenylene (25.6; $33._9$), 3, 4-benzophenanthrene (25.4; —) *p*-terphenyl (28.3; $47._9$), 1, 12-benzperylene (30.0; $40._7$), 3, 4-benztetraphene (32.6; $45._9$), 1, 2, 5, 6-dibenzanthracene (33.9; $49._3$), pentacene (37.7; $48._9$), picene (33.5; $45._9$), coronene (30.7; $36._9$), 1, 2, 4, 5-dibenzpyrene (32.9; $48._3$), 1, 2, 6, 7-dibenzpyrene (35.1; $45._6$), 1, 3, 5-triphenylbenzene (34.0; $55._6$), tetrabenzonaphthalene (33.9; $47._4$), isoviolanthrene A (52.2; $54._6$), violanthrene A (46.8; $48._1$), violanthrene B (36.7; $38._0$) and tetrabenzoperylene (28.2; $44._7$). The small values of ΔH for violanthrene B, tetrabenzoperylene and tetrabenzonaphthalene may reflect the existence of the non-coplanar structure of their molecules. Further, the large values of $\Delta S°$ for triphenylbenzene and terphenyl suggested the possibility of the rotation about their single bonds.

In 1952, we reported the enthalpy and the entropy of sublimation of polycyclic aromatic hydrocarbons, and found that there is rough additivity relation in the inner heats of sublimation among the compounds.

The general forces of the cohesion, or van der Waals' forces, between the polycyclic aromatic molecules play an important part in the building up of the aromatic crystals. Under these considerations, several workers have calculated the interaction energy of simple aromatic hydrocarbons by means of the approximation formula of Slater and Kirkwood for the van der Waals' forces.[1]

The agreement between the experimental (ΔH_{exp}) and theoretical (ΔH_{calc}) results, however, was not very good; ΔH_{exp} is 9.7 kcal/mol and ΔH_{calc} is 11.3 kcal/mol for benzene,[2] $\Delta H_{exp}=17.09$ kcal/mol, $\Delta H_{calc}=15.9$ kcal/mol for naphthalene[3] and $\Delta H_{exp}=22.30$ kcal/mol, $\Delta H_{calc}=25.23$ kcal/mol for anthracene.[3] This method for calculation may not be applied for the higher condensed aromatic hydrocarbons used in this work, because the calculation is too complicated and rough.

Recently, Craig *et al.* have discussed the relation between the crystal structure of the simple aromatic hydrocarbon and the intermolecular potential energy.[4] In their report, they concluded that the molecular arrangement in the crystal appears to depend upon minimized intermolecular hydrogen-hydrogen repulsion rather than upon the quadrupole-quadrupole interaction and also dispersion energies. These results suggest that we must consider the effect of hydrogen-hydrogen repulsion force when the calculation of intermolecular force in the crystal of aromatic hydrocarbons is carried out. These calculations of intermolecular force, however, are too complicated to extend to higher condensed aromatic hydrocarbons employed in this study.

In this report, we present experimental results of the vapour pressure measurements of some higher condensed aromatic hydrocarbons. Further, we will discuss the relation between intermolecular forces and molecular packing in crystal.

Experimental Methods

The vapour pressure of most crystalline organic substances is very low, usually much below one atmosphere, so that methods for measuring pressure in the range 10^{-2} to 10^{-5} torr have to be employed. In this study, we used the Knudsen effusion method, which is illustrated in Fig. 1 schematically. The sample under investigation was installed in a small cell of aluminum (8 mm in diameter, 7 mm in height), in a thermostat which was mounted in a highly evacuated chamber. In the chamber, the cell was suspended from a Cahn automatic electrobalance RG I with a silver string ($\phi=0.1$ mm). The cap of the aluminum cell had a carefully designed orifice of about

1) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).
2) J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).
3) I. Nitta, S. Seki and M. Momotani, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **71**, 430 (1950).
4) D. P. Craig, R. Mason, P. Pauling and D. P. Santry, *Proc. Roy. Soc.*, **A286**, 78 (1966).

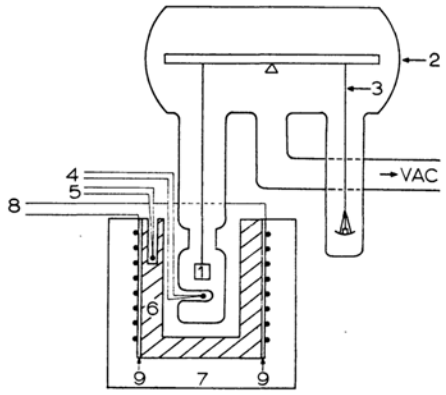

Fig. 1. The apparatus for measuring the vapour pressure by the effusion method.
1 Cell, 2 Electrobalance, 3 String, 4 Thermocouple, 5 Thermistor, 6 Cu block, 7 Asbestos, 8 Heater, 9 Mica

0.4 mm in diameter.*1 Under these conditions, the solid and vapour of the aromatic hydrocarbons remained in equilibrium while the vapour effused through the orifice. The rate of effusion (w/t) was obtained by determining the loss in weight of the cell. The vapour pressure was calculated by the following Knudsen equation,

$$p = \frac{w}{ts}\sqrt{\frac{2\pi \boldsymbol{R} T}{M}} \qquad (1)$$

where M is the molecular weight of the aromatic compound in vapour, T the absolute temperature, $\boldsymbol{R}$ the gas constant, s the area of the orifice and w is the mass effused through the orifice in t seconds. The cross section area of orifice s was 1.34×10^{-3} cm^2. The weight decrease of sample, effused through the orifice, per unit time was determined by means of the electrobalance, having the sensitivity of 0.002 mg in weight change.

The temperature of the furnace was controlled carefully; below 300°C a Takara thermistor-type temperature controller TR-11 (controlled to ±0.1°C) was used and above 300°C a Chino temperature controller S-175 (maintained ±0.5°C) was employed. The temperature of the cell was measured by a thermocouple as shown in Fig. 1.

Results

We found that a good linear relation is obtained between the logarithm of vapour pressure (p)

TABLE 1. THE HEATS OF SUBLIMATION OF POLYCYCLIC AROMATIC HYDROCARBONS

Substance	Number of C, H atoms	Molecular weight	Density	Mp and Bp		$\log p = A - \frac{B}{T}$ A	B	ΔH kcal/mol	$\Delta S°$ cal/mol·deg	$\Delta U°/n$
1,2-Benzanthracene	$C_{18}H_{12}$	228	1.245	158—159	437.6	12.72	6.33	28.8	44.8	1.60
Tetracene	$C_{18}H_{12}$	228	1.24	357	443	12.38	6.54	29.8	43.3	1.62
Chrysene	$C_{18}H_{12}$	228	1.27	255—256	441	12.32	6.16	28.1	43.0	1.53
Triphenylene	$C_{18}H_{12}$	228	1.28	196.5	438	10.31	5.62	25.6	33.9	1.41
*3,4-Benzophenanthrene	$C_{18}H_{12}$	228	1.26	68				25.4		1.38
p-Terphenyl	$C_{18}H_{14}$	230		208	400	13.39	6.21	28.3	47.9	1.55
1,12-Benzperylene	$C_{22}H_{12}$	276	1.35	273	>500	11.82	6.58	30.0	40.7	1.34
3,4-Benztetraphene	$C_{22}H_{14}$	278		294	514	12.95	7.15	32.6	45.9	1.46
1,2,5,6-Dibenzanthracene	$C_{22}H_{14}$	278	1.28	262	524	13.39	7.42	33.9	49.3	1.52
Pentacene	$C_{22}H_{14}$	278	1.30	>300		13.60	8.26	37.7	48.9	1.69
Picene	$C_{22}H_{14}$	278		364	518—520	12.95	7.35	33.5	45.9	1.50
Coronene	$C_{24}H_{12}$	300	1.38	438—440		10.98	6.74	30.7	36.9	1.26
1,2,4,5-Dibenzpyrene	$C_{24}H_{14}$	302		233—234		13.48	7.65	32.9	48.3	1.35
1,2,6,7-Dibenzpyrene	$C_{24}H_{14}$	302		340—342		12.88	7.70	35.1	45.6	1.44
1,3,5-Triphenylbenzene	$C_{24}H_{18}$	306	1.22	175.5	460	15.08	7.45	34.0	55.6	1.39
Tetrabenzonaphthalene	$C_{26}H_{16}$	328	1.29	215		13.27	7.43	33.9	47.4	1.28
Isoviolanthrene A	$C_{34}H_{18}$	426	1.51	510		14.85	11.45	52.2	54.6	1.52
Violanthrene A	$C_{34}H_{18}$	426	1.49	478		13.08	10.26	46.8	48.1	1.36
Violanthrene B	$C_{34}H_{18}$	426		330		11.76	8.05	36.7	38.0	1.06
Tetrabenzoperylene	$C_{34}H_{18}$	426		333		12.80	6.19	28.2	44.7	0.815

* A. Magnus, H. Hartmann and F. Becker, *Z. Physik. Chem.*, **197**, 75 (1951).

*1 The thickness of thin wall of the cap is less than 0.1 mm. Therefore, according to Clausing, the effect of size of the orifice on pressure p (Eq. (1)) is negligible. (P. Clausing, *Ann. Physik*, **12**, 961 (1932))

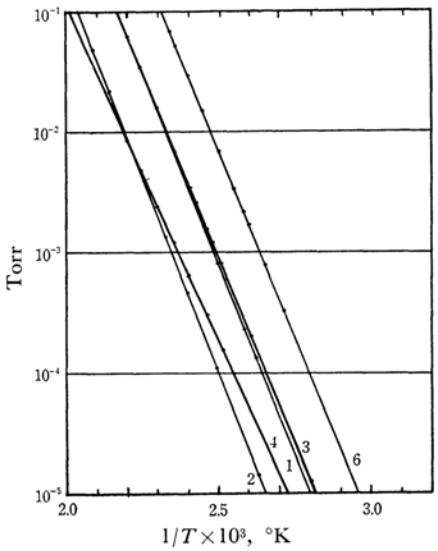

Fig. 2-1

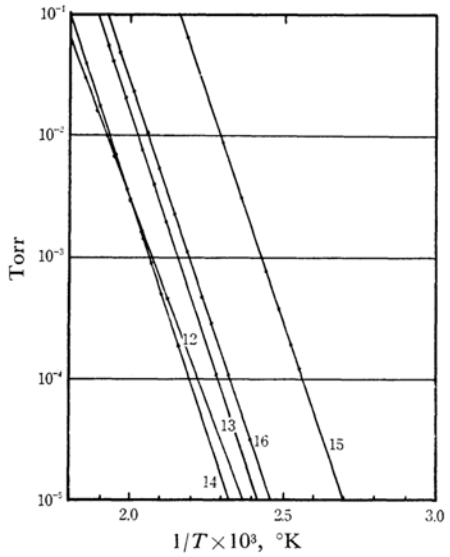

Fig. 2-3

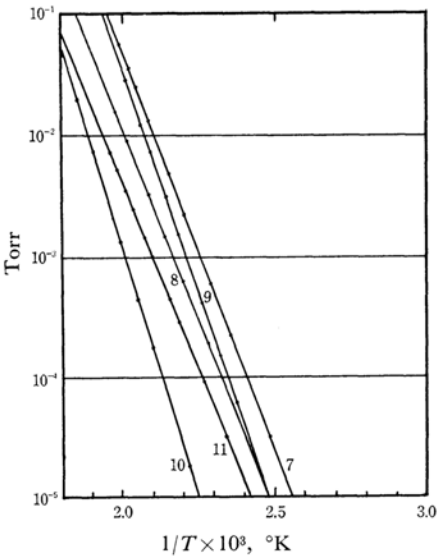

Fig. 2-2

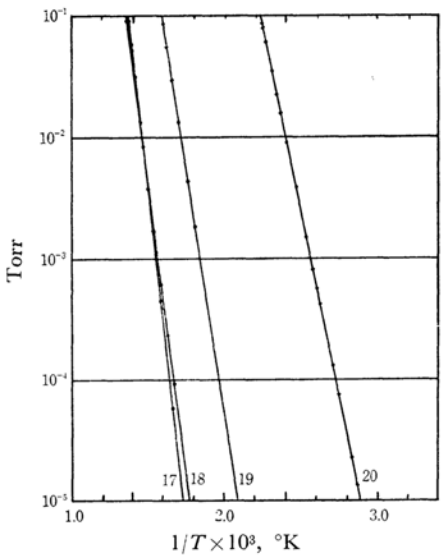

Fig. 2-4

Fig. 2. The vapour pressure of the polycyclic aromatic hydrocarbons.
1 1,2-Benzanthracene, 2 Tetracene, 3 Chrysene, 4 Triphenylene, 5 3,4-Benzphenanthrene (not indicated), 6 *p*-Terphenyl, 7 1,12-Benzperylene, 8 3,4-Benztetraphene, 9 1,2,5,6-Dibenzanthracene, 10 Pentacene, 11 Picene, 12 Coronene, 13 1,2,4,5-Dibenzpyrene, 14 1,2,6,7-Dibenzpyrene, 15 1,3,5-Triphenylbenzene, 16 Tetrabenzonaphthalene, 17 Isoviolanthrene A, 18 Violanthrene A, 19 Violanthrene B, 20 Tetrabenzoperylene.

and the reciprocal of temperature (T) for each compound. Figure 2 shows the relation for a number of aromatic hydrocarbons.

From the empirical equation of $\log p = A - B/T$, the heat of sublimation (ΔH) as well as the entropy of sublimation ($\Delta S°$) under an atmospheric pressure were calculated by the Clausius-Clapeyron's equation:

$$\Delta H = 2.303 \cdot \boldsymbol{R} \cdot B \text{ kcal/mol} \qquad (2)$$

and

$$\Delta S° = 2.303\, \boldsymbol{R}(A - 2.881) \text{ cal/mol·deg.} \qquad (3)$$

Table 1 summarizes the experimental results of the vapour pressure. In the second column of the table, the number of carbon atoms and also of hydrogen atoms in each molecule are shown and in the third and fourth columns the molecular weight and also the density of the hydrocarbon are listed. Further, in the fifth column, the melting

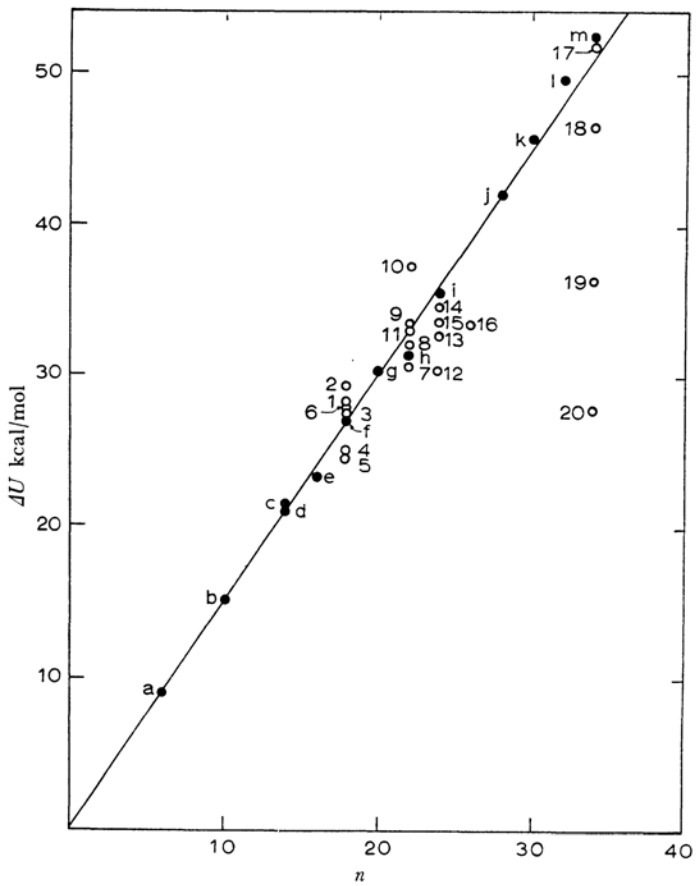

Fig. 3. The heats of sublimation plotted against the number of carbon atoms in a molecule. The numerical orders in the figure correspond to those in Fig. 2.
a Benzene, b Naphthalene, c Anthracene, d Phenanthrene, e Pyrene, f Tetracene, g Perylene, h Anthanthrene, i Coronene, j meso-Naphthodianthrene, k Pyranthrene, l Ovalene, m Violanthrene A.
These data, a—m, were obtained from Ref. 5.

point and boiling point of the compound are summarized. In the sixth, to ninth columns, the derived values of A, B, ΔH and ΔS ° are shown respectively. In the last column, are shown the values of inner heat of sublimation $\Delta U(=\Delta H-\boldsymbol{R}T)$ being assigned to one carbon atom. This relation is illustrated in Fig. 3, where the inner heats of sublimation are plotted against the number of carbon atoms in each molecule.

Discussion

Considerable theoretical interest in the inner heats of sublimation arises from the fact that it may be equated to the lattice energy of a compound. Previously, one of the authors (H. I.) reported that the lattice energy assigned to one carbon atom was 1.5 kcal/mol.[5] As is illustrated in Fig. 3,[*2] the inner heats of sublimation of the aromatic hydrocarbons which have 18, 22 and 24 carbon atoms (n) obey the empirical formula $\Delta U=1.5\,n$ kcal/mol roughly excepting those of coronene, tetracene and pentacene.

However, for the compounds with 34 carbon atoms, this formula is not satisfied; the experimental values of violanthrene B and tetrabenzoperylene are very different from the calculated value of the above empirical formula, 51 kcal/mol. Their inner heats of sublimation are much smaller than those of violanthrene A and isolviolanthrene A as listed in Table 1 and also their melting and boiling points are much lower than those of the latter. These large differences may be due to poor packing arising from non-coplanar structure of molecule as illustrated in Fig. 4.

The compounds having such a structure are

5) H. Inokuchi, S. Shiba, T. Handa and H. Akamatu, This Bulletin, **25**, 29 (1952).

*2 In the figure, the previous results (Ref. 5) are also illustrated as full circles.

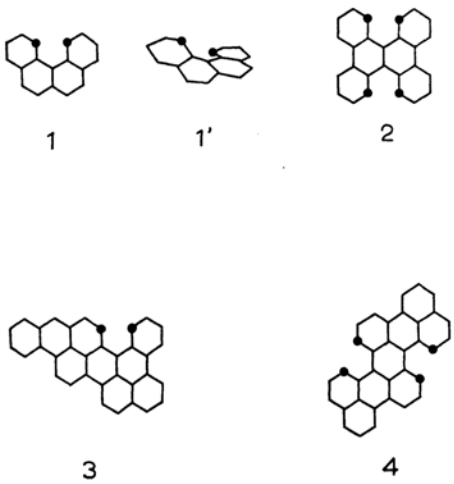

Fig. 4. The overcrowded compounds.
1 3,4-Benzophenanthrene (1′ its molecular model viewed at about 30° to the twofold axis), 2 Tetrabenzonaphthalene, 3 Violanthrene B, 4 Tetrabenzoperylene.
• is denoted the overcrowded carbon atoms.

denoted as "overcrowded" compounds.[6],*3 It was reported that an approach of 3.0 Å or less between non-bonded carbon atoms (mark • in Fig. 4) results in repulsion forces sufficient to produce detectable distortions within the molecule.[6] As the distortions within a molecule make the packing of the molecules loose in the crystal, it is expected that the inner heats and entropies of sublimation of the "overcrowded" compounds are smaller than the co-planar hydrocarbons having the same number of carbon atoms.

Large deviations from the ΔU *vs.* n plot were also observed for the other overcrowded compounds, tetrabenzonaphthalene and 3, 4 - benzophenanthrene. As is mentioned above, such discrepancy may also occur as a result of loose packing of the molecules in the crystal.

The cata-condensed aromatic hydrocarbons, tetracene and pentacene, have a fairly large lattice energy as is listed in Table 1. If part of these above-average lattice energies is produced from the energy transfer between the aromatic hydrocarbons, their higher conductivity in comparison with those of the similar aromatic hydrocarbons, as is shown in Table 2, may be interpretated.

Table 2. The electrical resistivity of the film of polycyclic aromatic hydrocarbons
(at room temperature)

Compound	Resistivity (Ω cm) at 15°C
Anthracene	10^{19}
Pyrene	10^{18}
Chrysene	10^{19}
Tetracene	10^{15}
Perylene	10^{17}
Pentacene	10^{14}
Anthanthrene	10^{18}
Coronene	10^{17}

The entropy of vaporization for triphenylbenzene and terphenyl is fairly larger than the corresponding quantities for the similar aromatic hydrocarbons. This anomaly may be due to the rotation about the single bond in the vapour phase as mentioned by Bradley for biphenyl.[8]

The authors wish to thank Dr. K. Amaya for his suggestion to make the apparatus. We also thank the Institute of Food Chemistry for grants to one of us (N. W.). The authors express their thanks to Mr. T. Takeda for fabricating the fine glass apparatus.

6) E. Harnik and G. M. J. Smidt, *J. Chem. Soc.*, **1954**, 3288, 3295, 3314.

*3 The refined crystallographic analysis of the overcrowded compounds used in this work, violanthrene B and tetrabenzoperylene, has not yet been completed.[7] However, we can expect that the molecular structures of these hydrocarbons are not completely co-planar in comparison with those of 3, 4-benzophenanthrene and also tetrabenzonaphthalene, which have already been analysed by the two dimensional Fourier method.[6] According to these results, the distance between the overcrowded carbon atoms 1 and 12 of 3, 4-benzophenanthrene (Fig. 4-1) is 3.0 Å; that is to say, the manner in which the molecule is distorted from planarity so as to achieve the separation between carbon atoms 1 and 12 may be seen in Fig. 4-1′.

7) T. Maekawa, Private communication.

8) J. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, **1953**, 1960.