The Density of the Polycyclic Aromatic Compounds

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It is already generally known that the physico-chemical properties of the polycyclic aromatic compounds are correlated closely to the number of carbon atoms comprised in the molecule. For instance, it has been found that the inner heat of sublimation of these hydrocarbons possesses a linear function of the number of carbon atoms with an average value of 1.5 kcal./mol. per carbon atom[1] and also that the increment of the number of benzene rings in the molecule of this series shows the increase of the electrical conductivity of these compounds[2].

These compounds belong to typical molecular crystal, in which molecules interact with each other by the van der Waals force. Lattice energies of crystals built up of homopolar molecules such as nitrogen or carbondioxide were first calculated by London[3]. The main object of this paper is to apply similar calculations of computing the density of the polycyclic aromatic compounds in comparison with the number of carbon atoms.

Experimental Procedures

The measurements of density for the polycyclic aromatic compounds were carried out at room temperature by means of the pycnometer as shown in Fig. 1. The total volume of this vessel, made of glass tubing of 15 mm. in diameter, was approximately 5 cc. The addition of the ground-on caps to cover the entrances of the vessel was helpful to prevent the evaporation of the pycnometer liquid.

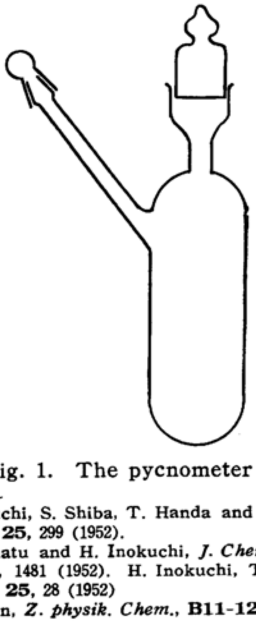

Fig. 1. The pycnometer

Since the solubility of violanthrene and *iso*-violanthrene in organic solvents is negligiblly small at room temperature, ethanol can be used as the pycnometer liquid. The solubilities of anthanthrene and naphthacene were, however, fairly high in the alcohol. Therefore, distilled water mixed with a very small amount of a surface-active agent was employed as the pycnometer liquid for these compounds.

Through a preliminary experiment, it was recognized that the adherence of bubbles of air on a surface of an organic compound was a serious reason for the fluctuation of the observed density values. In order to remove as much of the air as possible, the vessel containing the specimen and liquid had to be attached to a water-pump and to be kept under a reduced pressure.

The polycyclic aromatic compounds used in this experiment were purified thoroughly by the methods already described in previous reports[2].

Results and Discussion

The potential energy of a molecule as

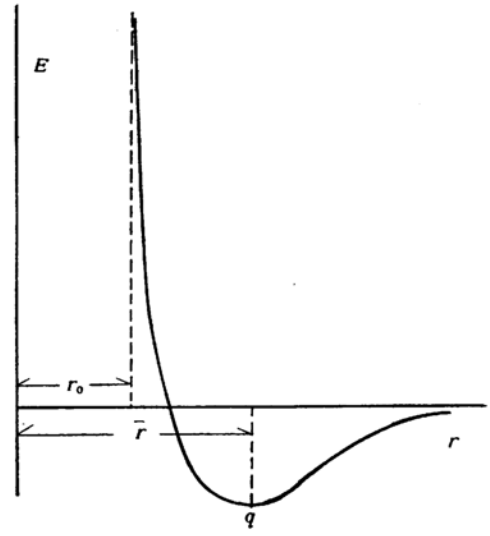

Fig. 2. The potential energy curve for intermolecular force.

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1) H. Inokuchi, S. Shiba, T. Handa and H. Akamatu, This Bulletin, **25**, 299 (1952).

2) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950); **20**, 1481 (1952). H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 28 (1952)

3) F. London, *Z. physik. Chem.*, **B11-12**, 222 (1930-1).

a function of an intermolecular distance, r, is generally expressed by a curve as shown in Fig. 2. This curve is made up of the sum of the dispersion and the repulsive force, the latter arising when the clouds of valence electrons of two molecules interpenetrate each other. These two forces are equal at the minimum point, q, of the potential energy curve. In addition, a strong repulsion due to the interpenetration of inner electron shells is assumed when the intermolecular distance is smaller than r_0. When the molecular weight of the hydrocarbon is very large, that is to say, the interaction between these molecules is very strong, it is reasonable to assume that the equilibrium distance between two molecules, $\bar{r}$, is nearly equal to r_0.

The molecule of the aromatic compound, a member of the series from benzene to graphite, has a plate-like shape, and is packed to make the molecules parallel to one another. Therefore, we can introduce the theory that r_0 corresponds to the interlayer spacing of graphite, 3.35Å, assuming that graphite is a kind of polycyclic aromatic compound having infinitely large molecular weight.

In calculating the sum of the dispersion forces and repulsive forces of atoms in the molecule, the contribution of hydrogen atoms may be neglected. Hence, the interation energy per one molecule $E(r)$ is expressed as,

$$E(r)=\frac{-AN^2}{(r-r_0)^6}+\frac{BN}{(r-r_0)^n} \tag{1}$$

in which N is the number of carbon atoms included in that molecule and A and B are constants.

At the equilibrium condition,

$$\left(\frac{\partial E(r)}{\partial r}\right)_{r=\bar{r}}=0=\frac{6AN^2}{(\bar{r}-r_0)^7}-\frac{nBN}{(\bar{r}-r_0)^{n+1}} \tag{2}$$

Therefore, $(\bar{r}-r_0)$ is represented as

$$(\bar{r}-r_0)^{n-6}=\frac{nB}{6A}\times\frac{1}{N} \tag{3}$$

The density of the aromatic compounds ρ is related to $\bar{r}$ by the equation

$$M/\rho=\boldsymbol{N}_A S\bar{r} \tag{4}$$

in which M and S are the molecular weight and the area of one molecule of the aromatic hydrocarbon respectively, and $\boldsymbol{N}_A$ is Avogadro's number.

Since M and S may be proportional approximately to N, the number of carbon atoms in that molecule, Equation 4 can be rewritten in the form

$$\begin{gathered}\bar{r}=C/\rho \\ C=M/\boldsymbol{N}_A\boldsymbol{S}=\text{constant}\end{gathered} \tag{5}$$

and also

$$r_0=C/\rho_\infty \tag{6}$$

Equation 3, therefore, becomes

$$\left(\frac{1}{\rho}-\frac{1}{\rho_\infty}\right)^{n-6}=\left(\frac{nB}{6AC^{n-6}}\right)\frac{1}{N} \tag{7}$$

This equation may be reduced to

$$\log\left(\frac{1}{\rho}-\frac{1}{\rho_\infty}\right)=-\frac{1}{n-6}\log N+\log Q \tag{8}$$

Here,

$$Q=nB/6AC^{n-6} \tag{9}$$

When we use the following numerical values

$\rho_\infty=2.26$ (density of graphite)

$n=8$

$B/AC^2=0.99$

in the above equation,

TABLE I

THE DENSITY OF POLYCYCLIC AROMATIC HYDROCARBONS

Compound	N	Density		Reference
		Observed	Calculated	
Benzene	6	1.04	1.02	
Naphthalene	10	1.15_2	1.16	4)
Anthracene	14	1.25	1.26	5)
Pyrene	16	1.27	1.29_5	6)
Naphthacene	18	1.33	1.33	
Tri-phenylene	18	1.3	1.33	7)
Perylene	20	1.35	1.36	
Benzperylene	22	1.35	1.38	8)
Anthanthrene	22	1.39	1.38	
Coronene	24	1.37_7	1.41	9)
Mesonaphthodianthrene	28	1.46	1.45	
Pyranthrene	30	1.47_5	1.46	
Ovalene	32	1.47_7	1.48	10)
Violanthrene	34	1.49	1.50	
Iso-violanthrene	34	1.50_5	1.50	
Circumanthracene	40	1.52	1.54	11)
Graphite	∞	2.26	(2.26)	

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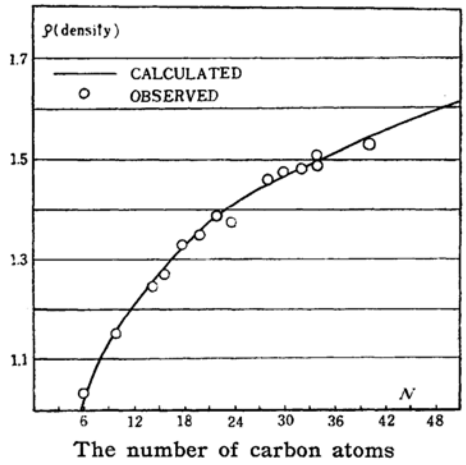

Fig. 3. The density of the polycyclic aromatic compounds.

$$\log\left(\frac{1}{\rho}-\frac{1}{2.26}\right)=-\frac{1}{2}\log N+0.120 \quad (10)$$

can be obtained.

The computed and also observed values of ρ are given in Table I and Fig. 3 for several polycyclic aromatic compounds. The agreement of these values in the table is satisfactory.

Table II
THE DENSITY OF CARBON BLACKS.

Specimen	L_a (Å)[12]	N	Density	
			observed	calculated
Royal Spectra	13.1	66	1.68	1.66
Philblack E	12.0	55	1.76	1.63
Peerless II-A	14.2	77	1.82	1.69
Tokyo Gas Carbon	13.4	69	1.68	1.67
Statex B	16.9	111	1.81	1.76
Philblack O	13.3	67	1.81	1.67

Applying Equation 10 to calculate the density of carbon blacks, we have the result in Table II. By means of the X-ray diffraction analysis, the dimension of a condensed polycyclic aromatic layer of the carbon, L_a, was calculated from the breadth of (10) reflection at half of the maximum intensity, applying Warren's formula for the random layer lattice. The area occupied by a carbon atom in the layer, may be assumed an equilateral triangle, for which b has the value of $a \sin 60°$, as illustrated in Fig. 4. Here, a possesses the distance of C−C bonding, 1.41Å. Thus, the number of carbon atoms in the layer is expressed

$$N=4L_a^2/3\sqrt{3}a^2 \quad (11)$$

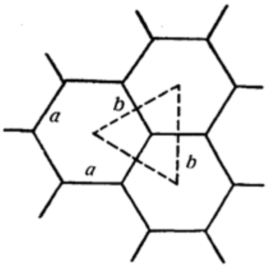

Fig. 4. The area occupied by a carbon atom in graphite layer.

On the basis of this table the authors are inclined to think that they have derived a relation between the density and the molecular weight of carbon blacks.

Summary

The density (ρ) of the polycyclic aromatic hydrocarbons, from benzene (C_6H_6) to circumanthracene ($C_{40}H_{16}$), are correlated closely to the number of carbon atoms (N) included in the molecule. We may be expressed the relation as $\log(1/\rho-1/\rho_\infty)=-(1/2)\log N+0.120$, in which ρ_∞ is the density of graphite, 2.26. The agreement of the computed values with the observed results is satisfactory. A trial to apply the equation to calculate the density of carbons is made with some success.

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