On the Diamagnetism of Perylene. I.

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S. Banerjee(1) has measured the principal diamagnetic anisotropies along the three principal axes on various aromatic crystals. The diamagnetic value of the perylene crystal can be found in his paper, and this may be the only experimental one which we can see in the literature on this substance before the World War II. According to his result, the mean value of the three principal susceptibilities per mole of perylene becomes -159.6×10^{-6}. It is interesting that not only does this value deviate widely from Pascal's additive law, but also, as Banerjee had already pointed out, the diamagnetic anisotropy of this molecule is almost the same in magnitude with that of pyrene. As there are some other questionable points in this problem and as we fortunately had a specimen of perylene at hand, this mesurement was newly attempted during the War. The result obtained by us showed somewhat larger diamagnetism than that of Banerjee's, and one of the values has already been published in another place briefly(2). During the preparation of this paper, we have found in Chemical Abstracts the experimental value of this substance, reported by Pacault(3) to be $\chi_M = -165.0\times10^{-6}$, where χ_M denotes mole susceptibility.

Synthesis of the Specimen and its Purification. The perylene used in this experiment had been prepared by the method of Hansgirg and Zinke(4) by Prof. Kazuya Murata at Hiroshima Technical College, to whom we owe very much. It had been recrystallized alternatively from benzene and glacial acetic acid four times, and directly before the measurement, it was recrystallized once more from glacial acetic acid. Its melting point was 264°–265°. A part of this sample sent to Zinke had been appreciated by him to be very pure.

Magnetic Measurements. We employed the apparatus of modified type of zero point method of Weiß und Foëx(5), applying the constant field strength of about 6,000 gauß. The mass susceptibility of powdered naphthalene which had been purified by several recrystallizations and

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(1) S. Banerjee, *Z. Krist.*, **100** (1939), 316.
(2) G. Hazato, *Kagaku (Iwanami)*, **14** (1944), 162, Table 3.
(3) A. Pacault, *Ann. chim.* [12], **1** (1946), 527; cf, *Chem. Abstracts*, **42** (1948), 4409
(4) F. Hansgirg and A. Zinke, *Monatsh*,, **40** (1919), 403.
(5) Refer, for example, to W. Klemm, "Magnetochemie," p. 46, Leipzig (1936).

sublimations, and that of purified water were chosen as standards, assuming their values to be -0.717×10^{-6} and -0.720×10^{-6}, respectively. The principle of this method lies in comparing the repulsive force, induced by the constant magnetic field in each gram of the specimen, with that of the standard substance, assuming the proportionality between the mass susceptibility and the corresponding repulsive force.⁽⁵⁾ Both naphthalene and specimen were powdered as fine as possible, and about 0.3 g. of each of them was crammed into the globular part of quartz vessel A, which is shown in Fig. 1. The vessel A is jointed to the end of the quartz tube B held horizontally by two bifilar suspensions⁽⁵⁾, and P shows the poles of the magnet. When A is connected to B, the two projections situated at each end of A and B are adjusted so as to be in contact with each other at the same position. In this manner, we can always reproduce the same relative position of the sample to the magnetic poles.

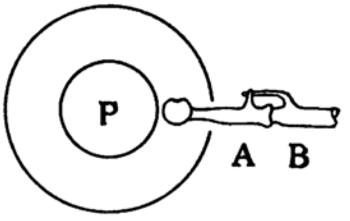

Fig. 1.

The repulsive force mentioned above can be measured by the magnitude of the counter force applied against the repulsive one so as to bring back the specimen to the original zero point by means of a weak direct current passed through the secondary coil which is situated at the other end of the quartz tube B⁽⁵⁾. The reading of the microammeter inserted in the circuit of the secondary coil ought to be proportional to the repulsive force, namely the product of the mass susceptibility and the weight of the sample.

The results obtained are as follows:

Table 1.

	Substance	Weight of Substance (g.)	Reading of Ammeter (μA.)	$-\chi_g\times10^6$	$-\chi_M\times10^6$
(a)	Water	0.4326	24.8	0.720 (standard)	
	Perylene	0 3530	19.0	0.676 (obtained)	170 4
(b)	Naphthalene	0.3136	17.7	0.717 (standard)	
	Perylene	0.3530	19.0	0.684 (obtained)	172.4

where χ_g and χ_M denote the mass and mole susceptibilities respectively.

Brief Considerations. If the configuration of perylene is considered to consist of two naphthalene nuclei combined at both the peri-positions, the magnetic susceptibility of this molecule may be calculated from that of naphthalene as follows:

$$\chi_M(\text{Perylene}) = 2\chi_M(\text{Naphthalene}) - 4\chi(\text{H})$$
$$= -171.8 \times 10^{-6}, \qquad (1)$$

assuming that,

$$\chi_M(\text{Naphthalene})^{(6)} = -91.77 \times 10^{-6}$$

and $$\chi(\text{H})^{(7)} = -2.93 \times 10^{-6}.$$

The value obtained in (1) coincides closely with our experimental ones shown in Table 1. Accordingly, we can say that the additive law is also nearly correct in the case of perylene, if we neglect the so-called "constitutive corrections for the trinuclear and the binuclear carbons" with regard to the central hexagon. This result shows that in perylene molecule the two naphthalene nuclei are playing a predominant role, and the central nucleus (C in Fig. 2) seems to have a special structure, having no correction term to be added for its own sake. If it were not so, the correction terms for the trinuclear carbons and for the binuclear ones would have to be added according to Pascal's additive law(7). If these corrections were added, the resulting value would become -185.2×10^{-6}, which lies far from the experimental one. As a matter of fact, however, it is natural to consider that the origin of the correction terms for "the trinuclear and binuclear carbons" may rather be ascribed to the conditions of the planar structure of the molecular orbits in aromatic network, than to the specific character of individual carbon atom.

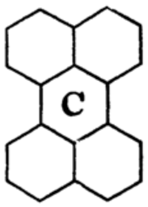

Fig. 2

On the other hand, it can be considered that aromatic molecule, in general, consists of two parts of diamagnetism, viz. the one is isotropic and the other anisotropic. The isotropic part will be represented by K_1 or K_2, showing the mole susceptibility of aromatic compounds when the molecular plane is situated parallel to the directions of the magnetic field; in this condition the anisotropic part vanishes. Let the anisotropic part per mole be ΔK, the following relationship will be satisfied,(8)

$$\Delta K = K_3 - K_1.$$

Here, K_3 represents the susceptibility when the molecular planes are put perpendicular to the direction of the magnetic field. Then in the case

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(6) International Critical Tables.

(7) Cf., for instance, S. S. Bhatnagar and K. N. Mathur, "Physical Principles and Applications of Magnetochemistry," p. 90-92, London (1935); W. Klemm, "Magnetochemie," p. 160-161.

(8) L. Pauling, *J. Chem. Phys.*, 4 (1936), 676.

of fine powdered crystals, the mean susceptibility per mole becomes

$$\chi_M = K_1 + \frac{1}{3} \varDelta K, \tag{2}$$

because of the planar structure of the molecule.

Accordingly, we can deduce $\varDelta K$ from the equation (2), knowing the numerical value of K_1. To evaluate K_1 approximately, it is convenient to use the following modification of Pascal's additive law :(9)

$$K_1 = \sum \chi(\mathrm{C}=) + \sum \chi(\mathrm{H}), \tag{3}$$

where, $\chi(\mathrm{C}=)$ denotes the atomic susceptibility of the unsaturated carbon including the constitutive correction of half a double bond; the numerical values are(7)

$$\left.\begin{aligned} \chi(\mathrm{C}=) &= \chi(\mathrm{C}) + \frac{1}{4}\lambda(\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}) \\ &= \left(-6 + \frac{1}{4} \times 10.56\right) \times 10^{-6} = -3.36 \times 10^{-6} \\ \chi(\mathrm{H}) &= -2.93 \times 10^{-6}. \end{aligned}\right\} \tag{4}$$

Applying these values in (3) and (2) in combination with the experimental values of χ_M, we can calculate $\varDelta K$ for various aromatic molecules. Taking the value of $\varDelta K$ of benzene as the unit, we can evaluate the relative anisotropies of various aromatic hydrocarbons, the results being summarized in Table 2 together with those by other authors(10)(11)

Table 2.

Substance	$-\chi_M \times 10^6$	Relative Anisotropies		
		Obs. (powd.)	Obs. (s.c.)(10)	Theo. (L.)(11)
Benzene	55.1	1	1	1
Naphthalene	91.8	2.0	2.11	2 18
Anthracene	129.2	3,05	3.38	3.45
Phenanthrene	127.9	2.97	3.07	3.19
Pyrene	147.9	3.74	4.31	4.46
Diphenyl	104.9	2.0	2.20	2.21

Here, Obs. (powd.) indicates the results obtained in the present case, and χ_M the experimental susceptibilities of powdered crystals or liquid obtained by Pascal. Obs. (s. c.) shows the results obtained by Lonsdale and Krishnan on the single crystals except in the case of benzene. Theo. (L.) shows the pure theoretical ones obtained by London.

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(9) G. Hazato, *J. Chem. Soc. Japan*, **64** (1943), 483.

(10) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A**, **156** (1936), 597.

(11) F. London, *J. de Physique*, 8 (1937), 397; *J. Chem. Phys.*, **5** (1937), 837.

In the analogous manner, we can deduce the relative anisotropy of perylene to naphthalene from the results of Table 1, i. e.

$$\Delta K \text{ (Perylene)}/\Delta K \text{ (Naphthalene)} = 1.96-2.02. \qquad (5)$$

This result coincides well with that of the relation (1). The relative anisotropic values shown in Table 2 correspond approximately with the number of benzene nuclei. And from this result it may analogously be deduced that ΔK of perylene is rather 2.5 times that of naphthalene, but contrary to the supposition, the result of observation indicates as if two naphthalene nuclei predominated in the perylene molecule. If the ΔK of perylene were 2.5 times as large as that of naphthalene, $-\chi_M \times 10^6$ of perylene would be 187, which deviates widely from the experimental one.

In spite of the above mentioned discussions, there still remain many questions which we have to discuss further in detail. It may be certain, however, that from the structural point of view, the perylene molecule has essentially two predominant naphthalene nuclei, of which both the peri-bonds are somewhat longer than that of the carbon bond in benzene nucleus, but are not pure single bonds. This argument will prove to be correct, if the theoretical treatment of London[(10)] is modified a little. Details of it will be mentioned in the following articles.

Summary.

The diamagnetic susceptibility of perylene in powdered form has been measured and found to be $-(171\pm1)\times10^{-6}$ per mole, and from this value the structure of perylene is discussed. A simple method has also been proposed to evaluate the anisotropic part from the mean molecular susceptibilities of aromatic molecules. The present result shows that perylene molecule has two predominant naphthalene nuclei and the central hexagon in this molecule has a special structure as compared with the other four.

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