On the Diamagnetism of Perylene. II*.

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In a preceding paper,(1) we have shown a simple method to compute the diamagnetic anisotropy of aromatic molecules from the experimental values of powdered crystals, and we have found that perylene molecule has an anisotropic part about twice as large as that of naphthalene.

In general, aromatic molecules show abnormally large diamagnetic anisotropy, the susceptibility being maximum if the direction of the impressed field is perpendicular to the molecular plane, and minimum if the two are parallel with each other. To explain this phenomenon, it was assumed by several authors(2) that in these molecules the diamagnetic currents might circulate from one atom to the other along the aromatic ring system. In other words, at each carbon atom, constituting the aromatic ring system, there is a π- or p_z-electron which is free to move, under the influence of the magnetic field, from one carbon atom to the adjacent one. This is closely analogous to the electric current induced in a conducting network. This hypothesis has come to be generally accepted in qualiative explanations.

Starting from the above consideration, quantitative interpretations of the anisotropic parts of the aromatic molecules have been worked out by Pauling(3) and by London(4). Pauling's argument is based essentially on classical ideas, assuming that the aromatic rings should behave like supraconductors.(5) London uses a quantum mechanical procedure, based on Hückel's molecular orbital treatment, extending to the case of the presence of a magnetic field. He calculated the ratios of the anisotropies of various condensed aromatic compounds to that of benzene, obtaining excellent agreement with experiment.

Here, in this paper, we shall apply the London theory to the theoretical calculation of the anisotropic part of perylene molecule, seeing how far the theory can carry us. The present calculation follows, for convenience' sake, the same notation and procedure as London's paper.(4)

London's secular equation is as follows:

$$|\eta_{kl} \exp\ 2\pi i f_{kl}) - x\,\delta_{kl}| = 0 \qquad (1)$$

Here $\eta_{kl}\begin{cases}1 \text{ if } k \text{ is a neighbor of } l\\ 0 \text{ if } k \text{ is not a neighbor of } l\end{cases}$ $\delta_{kl}\begin{cases}1 \text{ if } k = l\\ 0 \text{ if } k \neq l,\end{cases}$

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*) This paper was read at the annual meeting of the chemical constitution of the Chem. Soc. of Japan in Oct. 1946 and in Apr. 1948.

(1) H. Shiba, and G. Hazato, this Bulletin, **22** (1949), 92.

(2) P. Ehrenfest, *Physica*, **5** (1925), 388; *Z. Phys.*, **58** (1929), 719; C. V. Raman, and K. S. Krishnan, *Proc. Roy. Soc.* (*London*), **A, 113** (1927), 511; C. V. Raman, *Nature*, **123** (1929), 945; K. Lonsdale, *Proc. Roy, Soc.* (*London*), **A. 159** (1937), 149.

(3) L. Pauling, *J. Chem. Phys.*, **4** (1936), 673.

(4) E. London, *J. du Physique*, **8** (1937), 397.

(5) Cf. F. London, *J. Chem. Phys.*, **5** (1937), 837.

and
$$x = \frac{E^{(1)} - W_0}{W_1} \tag{2}$$

$E^{(1)}$ is the ordinary first order perturbation energy:

$$E^{(1)} = E - E^{(0)}\,, \tag{3}$$

$E^{(0)}$ is the energy of the zeroth order approximation under the influence of the magnetic field, which is expressed by

$$E^{(0)} = E^{(00)} + \frac{1}{2}\chi H^2, \tag{4}$$

where χ is the susceptibility contribution of the π-electron (one per aromatic carbon atom), and H is the field strength. In equation (2), W_o is the Coulomb integral independent of the magnetic field, W_1 is the ordinary exchange integral of the nearest neighbors of the orbital theory in the absence of the magnetic field, and in this case, this is used as a unit of the energy scale. In equation (1),

$$\exp\,(2\pi i f_{kl}) = W_{kl}/W_1 \tag{5}$$

and
$$f_{kl} = (e/hc)\, H\cdot S_{kl}, \tag{6}$$

in which W_{kl} represents the exchange integral in the presence of the magnetic field, S_{kl} is the area of the triangle formed by the neighbors k, l and the origin, arbitrarily chosen in the plane of the molecule, therefore, f_{kl} can be considered as a numerical value proportional to the magnetic flux.

Following the above conditions and the model shown in Fig. 1, the secular determinant of perylene molecule can be arranged in the form

$$\begin{array}{c|cccccccccccccccccccc|}
 & 0 & 1 & 2 & 3 & 4 & 0' & 4' & 3' & 2' & 1' & \bar{1}' & \bar{2}' & \bar{3}' & \bar{4}' & \bar{0}' & \bar{4} & \bar{3} & \bar{2} & \bar{1} & \bar{0} \\
0 & -x & \varepsilon_1^* & & & & 1 & & & & \varepsilon_1 & & & & & & & & & & \\
1 & \varepsilon_1 & -x & 1 & & & & & & & & & & & & & & & & \alpha\varepsilon_1^* & \\
2 & & 1 & -x & \varepsilon_2 & & & & & & & & & & & & & & & & \\
3 & & & \varepsilon_2^* & -x & \varepsilon_3 & & & & & & & & & & & & & & & \\
4 & & & & \varepsilon_3^* & -x & \varepsilon_2 & & & & & & & & & & & & & & \\
0' & 1 & & & & \varepsilon_2^* & -x & \varepsilon_2 & & & & & & & & & & & & & \\
4' & & & & & & \varepsilon_2^* & -x & \varepsilon_3 & & & & & & & & & & & & \\
3' & & & & & & & \varepsilon_3^* & -x & \varepsilon_2 & & & & & & & & & & & \\
2' & & & & & & & & \varepsilon_2^* & -x & 1 & & & & & & & & & & \\
1' & \varepsilon_1^* & & & & & & & & 1 & -x & \alpha\varepsilon_1 & & & & & & & & & \\
\bar{1}' & & & & & & & & & & \alpha\varepsilon_1^* & -x & 1 & & & & & & & & \varepsilon_1 \\
\bar{2}' & & & & & & & & & & & 1 & -x & \varepsilon_2 & & & & & & & \\
\bar{3}' & & & & & & & & & & & & \varepsilon_2^* & -x & \varepsilon_3 & & & & & & \\
\bar{4}' & & & & & & & & & & & & & \varepsilon_3^* & -x & \varepsilon_2 & & & & & \\
\bar{0}' & & & & & & & & & & & & & & \varepsilon_2^* & -x & \varepsilon_2 & & & & 1 \\
\bar{4} & & & & & & & & & & & & & & & \varepsilon_2 & -x & \varepsilon_3 & & & \\
\bar{3} & & & & & & & & & & & & & & & & \varepsilon_3^* & -x & \varepsilon_2 & & \\
\bar{2} & & & & & & & & & & & & & & & & & \varepsilon_2^* & -x & 1 & \\
\bar{1} & & \alpha\varepsilon_1 & & & & & & & & & & & & & & & & 1 & -x & \varepsilon_1^* \\
\bar{0} & & & & & & & & & & & \varepsilon_1^* & & & & 1 & & & & \varepsilon_1 & -x
\end{array} = 0\,, \tag{7}$$

in which $\varepsilon=\exp(2\pi i f_{kl})$ and $\varepsilon^*=\exp(-2\pi i f_{kl})$. For convenience' sake, we may prefer ε to ε^*, in case of the clockwise rotation about the center of the central hexagon.

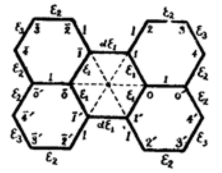

Fig. 1.

The determinant is of even degree in x, and it follows that the roots of x occur in pairs of type $\pm x$. It also follows that, as we see in Fig, 1, the model has symmetrical operation of inversion at the center of the central hexagon. In such a case, the determinant can be tansformed in general to one of the type

$$\left|\begin{array}{c:c} \Delta_1 & 0 \\ \hdashline 0 & \Delta_2 \end{array}\right| = 0.$$

Accordingly, equation (7) can be separated into the solution of two determinants, namely

$$\Delta_1=\begin{vmatrix}
-x & \varepsilon_1^* & & & & 1 & & & & \varepsilon_1 \\
\varepsilon_1 & -x & 1 & & & & & & & \alpha\varepsilon_1^* \\
 & 1 & -x & \varepsilon_2 & & & & & & \\
 & & \varepsilon_2^* & -x & \varepsilon_3 & & & & & \\
 & & & \varepsilon_3^* & -x & \varepsilon_2 & & & & \\
1 & & & & \varepsilon_2^* & -x & \varepsilon_2 & & & \\
 & & & & & \varepsilon_2^* & -x & \varepsilon_3 & & \\
 & & & & & & \varepsilon_3^* & -x & \varepsilon_2 & \\
 & & & & & & & \varepsilon_2^* & -x & 1 \\
\varepsilon_1^* & \alpha\varepsilon_1 & & & & & & & 1 & -x
\end{vmatrix}=0 \quad \text{and} \quad \Delta_2=\begin{vmatrix}
-x & 1 & & & & & & & -\alpha\varepsilon_1^* & \varepsilon_1 \\
1 & -x & \varepsilon_2 & & & & & & & \\
 & \varepsilon_2^* & -x & \varepsilon_3 & & & & & & \\
 & & \varepsilon_3^* & -x & \varepsilon_2 & & & & & \\
 & & & \varepsilon_2^* & -x & \varepsilon_2 & & & & 1 \\
 & & & & \varepsilon_2^* & -x & \varepsilon_3 & & & \\
 & & & & & \varepsilon_3^* & -x & \varepsilon_2 & & \\
 & & & & & & \varepsilon_2^* & -x & 1 & \\
-\alpha\varepsilon_1 & & & & & & & 1 & -x & \varepsilon_1^* \\
\varepsilon_1^* & & & & 1 & & & & \varepsilon_1 & -x
\end{vmatrix}=0.$$

Expanding Δ_1 or Δ_2, and after some approximation,(4) we have

$$(x^2-1)\{x^8-10x^6+31x^4-34x^2+9-\alpha^2(x^6-6x^4+8x^2)\mp 2\alpha(x^5-5x^3+7x)\}$$
$$+\frac{1}{4}(2\pi f)^2\{8x^4-24x^2+24\pm\alpha(x^7-6x^5+28x^3-15x)\} = 0. \qquad (8)$$

Where

$$f=(e/hc)\cdot H\cdot S_B, \qquad (9)$$

S_B = the area of each hexagon.

In equations (7), (8) and in Fig. 1, α is a parameter which can take on the fractional values from zero to 1. That is, if $\alpha=1$, all the hexagons are equally regular ones, and the method is identical with London's general procedure, but in the case of $\alpha=0$, both $1\bar{1}$ and $1'\bar{1}$ (Fig. 1) are pure single bonds, generally speaking, αW_1 represents the exchange integral in $1\bar{1}$, or $1'\bar{1}'$ bond, and in the other places, we can put it equally as W_1 whose value is the same as that of the benzene ring.

Now let x_p be a root of equation (8). From the relation (2) we have

$$E_p^{(1)} = W_0 + x_p W_1. \qquad (10)$$

Substituting (4) in (3), and by means of the partial differentiation with regard to H, a susceptibility contribution of a π-electron becomes

$$\chi_p = -\left(\frac{\partial^2 E^{(1)}}{\partial H^2}\right)_{H\to 0} \tag{11}$$

Since equation (8) has the form: $F_1\ (x) + (2\pi f)^2 \cdot F_2\ (x) = 0$, let x' be a root of $F_1\ (x) = 0$, and the corresponding root of (8) will be expressed approximately by

$$x = x' + x''\ (2\pi f)^2, \tag{12}$$

in which

$$x'' = \frac{F_2(x')}{F_1'(x')},$$

F_1' represents the first derivative of F_1 with regard to x.

From (9), (10), (11) and (12), we obtain London's final result:

$$\Delta\chi = 2\sum_{p=-\frac{N-2}{4}}^{\frac{N-2}{4}} \chi_p = -4\sum(x'')\ |\ W_1|\left(\frac{2\pi e S_B}{hc}\right)^2. \tag{13}$$

Here, the half of the lowest levels is completely occupied by all the electrons in question, so that each level may be occupied by a pair of electrons, each pair having antiparallel spin directions.

In equation (13), we can take both W_1 and S_B as constants throughout the model constructed by the same regular hexagons. But, in the present case, as is the case with Fig. 1 or equation (8), the area S_B of the central hexagon would be somewhat affected by α, that is, the distance $1\bar{1}$ or $1'\bar{1}'$ would be a function of α; the smaller the value of α becomes, the larger the S_B becomes. In spite of this fact, as it will be shown in a later paper, there is enough reason why we can ignore the S_B-effect of the central hexagon. Consequently, assuming W_1 and S_B to be constants, $\Delta\chi$ must directly be proportional to $\Sigma(x'')$; moreover, even if we take the parameter α as a variable, the corresponding values of $\Sigma(x'')$ may depend almost entirely upon the values of α only.

Now, all we have to do is to compute each numerical value of $\Sigma(x'')$ for each value of α. The solutions of equation (8) are shown in Table 1.

The notation x''' in the table represents the corresponding value of x'' in the case of the presence of non-orthogonality of 25% between the adjacent atomic wave functions, being computed by means of the approximate method of Brooks⁽⁶⁾. In the case of naphthalene each value of

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(6) H. Brooks, *J. Chem. Phys.*, **9** (1941), 463.

Table 1.

$\alpha = 0.3$	
$-x'$	x''
0.51728	+0.2552
0.73243	+0.5751
1	−0.2564
1	−0.4762
1.20736	+0.0085
1.39765	+0.4770
1.58274	−0.3989
1.66759	−0.0008
2.25520	+0.0142
2.36492	+0.0437
Σ; 13.725	+0.2414

$\alpha = 0.4$		
$-x'$	x''	x'''
0.48745	+0.2312	+0.1837
0.77230	+0.6983	+0.4905
1	−0.2381	−0.1524
1	−0.5555	−0.3555
1.17607	−0.0626	−0.0373
1.42843	+0.6431	+0.3492
1.57327	−0.5625	−0.2897
1.68842	+0.0340	+0.0168
2.24194	+0.0060	+0.0024
2.38958	+0.0463	+0.0182
Σ; 13.757	+0.2402	+0.2259

$\alpha = 0{,}8$		
$-x'$	x''	x'''
0.38709	+0.1656	+0.1377
0.92925	+2.4810	+1.6337
1	−0.1852	−0.1185
1	−1.6666	−1.0666
1.05604	−0.8037	−0.5030
1.54312514133	+349.0068	+181.7375
1.54341698022	−348.9217	−181.6741
1.80125	+0.1517	+0.0721
2.19881	−0.0456	−0.0190
2.51173	+0.0512	+0.0193
Σ; 13.97	+0.2335	+0.2191

$\alpha = 1{,}0$	
$-x'$	x''
0.34729	+0.1442
1	0
1	−0.1666
1	− ∞
1	− ∞
1.53209	+1.7428
1.59357	−1.6544
1.87938	+0.2176
2.18194	−0.0983
2.58836	+0.0509
Σ; 14.122	− ∞

$\Sigma(x'')$ and $\Sigma(x''')$ amounts to 0.1214(4) and 0.1144(6) respectively. Thus, we have in Table 2 the relative anisotropies of perylene, with regard to α, taking naphthalene as a unit.

Table 2.

α	0.0	0.3	0.4	0.8	1.0
$\Delta\chi$ (pery.)/$\Delta\chi$ (naph.)					
in orthogonal	2.0	1.99	1.97_8	1.92	− ∞
in non-orthogonal	2.0	—	1.97_6	1.91_5	− ∞
$\Sigma\,(-x')$	13.68	13.72	13.76	13.97	14.12

We can see from Table 2 that the effect of non-orthogonality is negligibly small.(7)

The results in Table 2 are graphically shown in Fig. 2, from which we obtain the following conclusions:

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(7) cf. reference (6).

1. In case of $\alpha=1$, $\Sigma(x'')$ has no definite value.
2. The increase in value of α is accompanied by the increasing of the double bond character in $1\bar{1}$- or $1'\bar{1}'$-bond, and at the same time the total binding energy between the corresponding π-electrons, viz. $2\Sigma(-x')$ increases. This result is a matter of course.

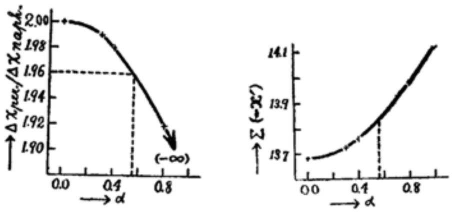

Fig. 2.

3. On the other hand, the increase of α reduces the diamagnetic anisotropy, and in the extreme case of $\alpha=0$, each $1\bar{1}$ or $1'\bar{1}$ being a pure single bond, the relative anisotropy is just equal to 2.0. This result is interesting; however, the alteration of the relative anisotropy with regard to α is very small except in the cases of $\alpha=0.9$ and 1.0 The experimental relative anisotropies in the preceding paper, being 1.96 and 2.02, lie within the range of $\alpha=0.0$ and 0.6.

In the special case of $\alpha=1$, as we see in Table 1, we have $x''=-\infty$ twice and $x''=0$ once, the latter representing a level which is not affected by the magnetic field. It is possible to consider that such unacceptable results may be ascribed to the quadruple roots of $x'=\pm1$, or to the highest symmetry of the model constructed with the same, five regular hexagons. As a matter of fact, it must be true that every carbon atom in aromatic rings, in general, cannot always be the same, except in the case of benzene. Therefore, there is a sufficient reason for omitting the case of $\alpha=1$ in this problem. Moreover, it must be borne in mind that the method of molecular orbitals neglects the r_{12} repulsion effects except in so far as it is represented by the Hartree's selfconsistent field, with the result that the multiple or ionic structure occurs with an excessive probability.(8) As the result of the same reason above, the $\Sigma(x')-\alpha$ curve in Fig. 2 is represented only by the attractive term wanting the repulsive one. In spite of such crudeness, the London theory is able to carry us to such a good agreement with experiment, so far from giving any discrepancy except the neighbors of $\alpha=1$.

On the other hand, however, according to Pauling's semi-classical theory, the diamagnetic anisotropy of perylene molecule has been shown to be about three times as large as that of naphthalene.(3) As pointed out by London (4), (5), the classical theory itself may be so far from giving any London (4), (5), the classical theory itself may be so far from giving any sufficient explanation about the diamagnetic anisotropy.

If we assume the model in Fig. 1 to be a peripheral form, in which we neglect the interactions between the π-electrons within the 10; 00'; 01'; $\bar{1}\bar{0}$; $\bar{0}\bar{0}'$ and $\bar{0}\bar{1}'$ bonds, we can easily derive the general formula from

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(8) cf. J. H. Van Vleck, and A. Sherman, *Rev. Mod. Phys.*, **7** (1935), 170.

the London theory as follows:

$$\Delta\chi_S/\Delta\chi_{\mathrm{Benz.}} = (6\times n/N)^2 \times \sin\frac{\pi}{6} \Big/ \sin\frac{\pi}{N},$$

where

$$n = \frac{\text{the total area of the model in problem}}{\text{the area of benzene}},$$

and N is the number of π-electrons along the periphery. Putting $n=5$ and $N=18$, $\Delta\chi_{\mathrm{pery.}}/\Delta\chi_{B.}$ becomes 7.98, and in the case of $n=5$ and $N=20$, the corresponding value becomes 7.19. Both of them are far from being realized in experiment.

Summary

Applying London s theory of diamagnetic anisotropy, computations have been performed on the structure of perylene molecule. In this problem, the theory gives no definite value if we choose such a model constructed with the same, five regular hexagons as we usually do in the conventional method. Introducing a simple parameter, this difficulty is removed with the result that the relative diamagnetic anisotropy of this molecule is about twice as large as that of naphthalene, showing a good agreement with experiment. A model as a peripheral form gives a divergent result from experiment.

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