

Supraconductivity in Aromatic Compounds

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Supraconductivity in Aromatic Compounds

The abnormally large values of the diamagnetic anisotropy of bismuth, graphite and particularly of the aromatic compounds have already led to the hypothesist that in these substances the diamagnetic currents might not be restricted, as usually, to the individual atoms but might circulate from one atom to the other along orbits of considerable length, e.g., along the aromatic rings. To this hypothesis I have recently given a theoretical basis, developing a theory which may be considered as the extension of the so-called "molecular orbital theory" to the case of the presence of a magnetic field.2 It could be shown why these interatomic currents are essentially restricted to the aromatic ring-systems and why they cannot appear in the interior of saturated molecules nor, as intermolecular currents, between saturated molecules.3 If one considers only interactions between neighboring atoms, the wave equation for the single electronic wave function c_k and energy E can be written in the form (the index k denotes the different aromatic C atoms):

$$\sum_{k} c_{k} [\eta_{kl} W_{1} e^{2\pi i f_{kl}} + \delta_{kl} (W_{0} - E)] = 0.$$
 (1)

Here

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

 W_1 is the ordinary exchange integral of neighbors of the orbital theory,

 W_0 is the coulombian integral,

 $f_{kl} = (e/hc)HS_{kl}$ where H is the external magnetic field and S_{kl} is the area of the triangle formed by the neighbors k, l and a zero point, arbitrarily chosen in the plane of the molecule.

We consider the distances between neighboring aromatic C atoms as equal, so that we have to deal with only one value W_1 for the exchange integral.

By means of Eq. (1) I have calculated³ the relative anisotropies $\Delta\chi$ of the diamagnetic susceptibility for various aromatic molecules, taking the anisotropy of benzene as unit. The results are listed in Table I, together with the experimental values given by Lonsdale⁴ ($\Delta\chi_{\rm benz}$. =54·10⁻⁶). Our calculation makes no use of any adjustable parameter; the theoretical values of the second column are a direct consequence of Eq. (1). If one wants to obtain the ex-

Table I. Relative diamagnetic anisotropies $(\Delta \chi / \Delta \chi_{\rm benz.})$

| | $(\Delta \chi/\Delta \chi_{\rm benz.})$ exper. | $(\Delta \chi/\Delta \chi_{\rm benz.})$ theor. | $(\Delta \chi/\Delta \chi_{ m benz})$ semi-class. |
|--|--|--|---|
| Naphthalene C ₁₀ H ₈ | 2.11 | 2.18 | 2.40 |
| Anthracene C ₁₄ H ₁₀ | 3.38 | 3.45 | 3.88 |
| Phenanthrene C ₁₄ H ₁₀ | 3.07 | 3.04 | 3.88 |
| Pyrene C ₁₆ H ₁₀ | 4.32 | 4.46 | 6.92 |
| Diphenyl C ₁₂ H ₁₀ | 2.20 | 2.21 | 2.00 |

perimental absolute value $\Delta \chi_{\rm benz} = 54 \cdot 10^{-6}$ for the anisotropy of benzene with a C-C distance of 1.39A, the exchange integral W_1 must have the value

$$W_1 = 4.4 [e \cdot \text{volts}].$$

About a year ago, in a paper published in this journal, Pauling¹ tried to calculate the diamagnetic anisotropies of aromatic compounds, taking as a basis the hypothesis that in these compounds the "aromatic" electrons can freely circulate around the aromatic rings. We can represent Pauling's calculus in a very simple way stating that the aromatic compounds shall behave like supraconductors, i.e., that for any cyclic way in the molecule the following equation5 holds:

$$\lambda \oint i_s ds = -\int \int H_n d\sigma$$
 (i = intensity of current). (2)

Applying this equation to any cyclic way and postulating in addition the conservation of electricity at any ramification, one obtains just as many relations as necessary for unambiguously calculating the distribution of current. The constant λ must have the value

$$\lambda = 1.12 \cdot 10^{-6} [sec./cm]$$

if one wants to obtain the experimental value $\Delta \chi_{\rm benz}$. = $54 \cdot 10^{-6}$ for the anisotropy of benzene, assuming an effective area of 5.10⁻¹⁶ cm² for the hexagon of that molecule.

The theory characterized by (2) can be considered as a kind of "semi-classical" analog of (1), insofar as it could be shown3 that for the limiting case of cyclic molecules of an infinite number of atoms, the two theories become identical. But for the real aromatic molecules this limiting case is very far from being realized. That is clearly demonstrated by the values listed in Table I under "semiclassical," which show great deviations from the experimental values as well as from the theoretical ones.

In order to make up for these deficiencies Pauling introduces a series of corrections which he attributes to variations of the electronic density and of the curvature and length of the links in the different aromatic compounds. I could not comprehend why all these effects should have such a great influence upon the susceptibility, as assumed by Pauling, and I thought it reasonable to consider none of them for a preliminary discussion. Accordingly in Table I the uncorrected values of both theories are compared. The application of corrections like those considered by Pauling seems to me scarcely compatible with the actual exactitude not only of the theoretical calculations but also of the measurements.

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 ⁵ F. and H. London, Physica 2, 341 (1935), Eqs. (8) (9).