

Proceedings of the Twenty-seventh Indian Science Congress.

Part II.

Issued 29th April, 1940.

TWENTY-SEVENTH INDIAN
SCIENCE CONGRESS

MADRAS, 1940

PRESIDENTIAL ADDRESS

Section of Physics

THE DIAMAGNETISM OF THE MOBILE
ELECTRONS IN AROMATIC MOLECULES

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Presidential Address

(*Delivered on Jan. 4, 1940*)

THE DIAMAGNETISM OF THE MOBILE ELECTRONS IN AROMATIC MOLECULES

Considerable progress has been made during recent years in our understanding of the structures of aromatic molecules, and in particular of benzene. Much of this progress is due, on the theoretical side, to the application of quantum mechanics to study the nature of the linkage between the carbon atoms in the benzene ring and the part played by the valency electrons in the linkage, and on the experimental side, to the detailed investigations on the Raman and the infra-red spectra of benzene and its deuterio-isomers, which have established the symmetry properties of benzene and the nature of its vibrations. One important result that emerges from these structural studies on benzene is that one electron in each carbon atom in the ring is mobile and is more or less free to migrate from atom to atom over the whole of the ring, a result of great significance to the sixty-year-old controversy regarding the location of the extra bonds in the benzene ring.

These mobile electrons have interesting magnetic properties, and I propose in this address to discuss some of these properties. In many respects the magnetic behaviour of these electrons is not dissimilar to that of the free electrons in metals, and the theoretical treatment in the two cases follows nearly the same course. I shall therefore deal first with the properties of free electrons, which are simpler.

THE PARAMAGNETISM OF AN ELECTRON GAS

All the characteristic properties of a metal are explained satisfactorily on the assumption that a certain number of electrons get detached from their atoms and are free to migrate from atom to atom throughout the metal. Taking for example the alkali metals, there is considerable evidence from their optical properties, their Hall coefficients, the fine structure of their emission spectra in the soft X-ray region, theoretical studies on metallic cohesion, etc., to show that the number of such free electrons should be just one per atom. The paramagnetic

properties of these electrons, regarded as forming a free-electron gas, are easily investigated. In the magnetic field the spin-moments of the electrons will place themselves either parallel or anti-parallel to the field, the number with parallel orientations preponderating, because of their lower energy in the field. Assuming that the preponderance of the parallel spins over the anti-parallel ones is determined by the classical statistics of Boltzmann, the susceptibility per unit volume of the gas will be given by the Curie law

$$\kappa_p = \frac{n\mu^2}{kT}, \quad \dots \quad (1)$$

where n is the number of electrons per unit volume, μ is the Bohr magneton, and the other letters have their usual significance.

In order, however, that the classical statistics may be applicable, the uncertainty Δq in the location of the position of the electron, which is determined by the Heisenberg relation

$$\Delta q \approx h / \Delta p \approx h / (mkT)^{1/2},$$

should be much less than the average distance between neighbouring electrons in the metal, namely $n^{-1/3}$. This would be the case only at temperatures much higher than

$$T_0 \approx \frac{h^2 n^{2/3}}{mk}.$$

For the alkali metals, with the number of free electrons equal to one per atom, this temperature will be of the order of 10^5 degrees. Hence at all ordinary temperatures the electron gas in these metals will be almost completely degenerate, and the electrons will occupy, in pairs with opposite spins, all the energy levels permitted by Pauli's Exclusion Principle, up to $E \approx kT_0$. A few stray electrons having energies near about kT_0 will occupy their energy levels singly. To put it more precisely, the energy distribution of the electrons will conform to the statistics of Fermi and Dirac.

Now it is only the few stray electrons which occupy their energy levels singly, that can orient in the magnetic field and contribute to the magnetic moment. Their number, n' per unit volume, will obviously be much smaller than n , roughly in the ratio of T to T_0 , and the susceptibility will therefore be given by the expression

$$\kappa_p = \frac{n'\mu^2}{kT} \approx \frac{n\mu^2}{kT_0}.$$

This gives the order of magnitude only. Detailed calculation gives for the spin-susceptibility of the degenerate gas

$$\kappa_p = \frac{3}{2} \frac{n\mu^2}{kT_0}, \quad \dots \quad (2)$$

where T_0 , the degeneracy temperature, is given by

$$T_0 = \frac{h^2}{8mk} \left(\frac{3n}{\pi} \right)^{2/3} \dots \dots \dots (3)$$

This in outline is the celebrated explanation given by Pauli for the feeble, temperature-independent paramagnetism exhibited by the alkali metals, which initiated the modern theories of the properties of electrons in metals.

THE DIAMAGNETISM OF A FREE-ELECTRON GAS ON THE CLASSICAL THEORY

That on the pure classical theory a free-electron gas should have no diamagnetism at all, seems to have been first demonstrated by Bohr. This result is at first sight surprising, since in the magnetic field the electrons will all describe paths whose projections on a plane perpendicular to the direction of the field will be circles, and the direction of motion in all the circles will be the same, and such as to give a negative moment along the direction of the field. On more careful consideration, however, it will be seen that the outer electrons in the medium which are too close to the boundary wall to execute complete circles will be reflected repeatedly from the wall, as shown in the diagram, (in which the boundary is assumed to be cylindrical),

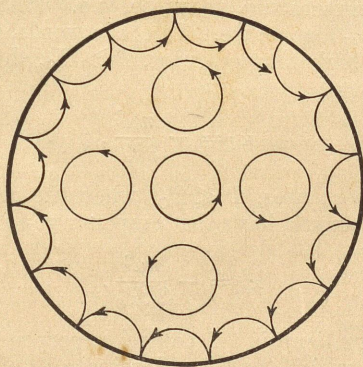


FIG. 1.

and will describe cuspidal paths; obviously this is equivalent to a creeping of these electrons along the boundary wall in a direction opposite to the direction of motion of the inner electrons. Though the creeping will be slow, yet because of the very large orbits in which these electrons creep, their contribution to the magnetic moment will be considerable, and on calculation we

find that it exactly neutralizes the diamagnetic contribution from the inner electrons.

This null result is independent of the nature of the boundary; in fact the boundary may be removed altogether. The result is even more general, and is applicable, as Miss van Leeuwen has demonstrated, not only to an electron gas, but to any dynamical system obeying pure classical statistics. The success of Langevin's apparently classical theory of diamagnetism, which explains so elegantly the diamagnetic properties of atoms and molecules, is due to the initial assumption of well-defined electronic orbits, which is a quantum result.

LANDAU'S DISCOVERY

To Landau we owe the discovery that if the motions of the free electrons in the magnetic field are quantized, as they should be according to our quantum mechanical ideas, the balancing between the diamagnetic moments of the inner electrons which execute uninterrupted paths, and the apparently paramagnetic contributions of the boundary electrons, is disturbed, much in favour of the former, and the result is a large diamagnetic moment. The argument by which the result is deduced is somewhat difficult to appreciate intuitively, and I shall therefore merely quote Landau's result, which has been checked by others, and with other models too. The diamagnetism of the free-electron gas is found to be just one-third of its spin-paramagnetism, whatever the temperature may be, i.e. whether the gas is degenerate or non-degenerate. In other words, the diamagnetic susceptibility at high temperatures, $T \gg T_0$, should conform to the Curie law

$$\kappa_d = -\frac{n\mu^2}{3kT}, \quad \dots \dots \dots (4)$$

and at low temperatures, $T \ll T_0$, when the gas is degenerate, the susceptibility should have the temperature-independent value

$$\kappa_d = -\frac{n\mu^2}{2kT_0}. \quad \dots \dots \dots (5)$$

The diamagnetism is of course superposed on the spin-paramagnetism, which will predominate, and the resultant susceptibility will be given by

$$\kappa = \kappa_p + \kappa_d.$$

EXPERIMENTAL VERIFICATION OF LANDAU'S DIAMAGNETISM

It would be of great interest to verify experimentally Landau's result, which is essentially a quantum result and has no counterpart in the classical theory. There are, however, two

serious difficulties in verifying this diamagnetism, firstly the predominant paramagnetism with which it is normally associated, and secondly the enormous degeneracy temperatures for the free electrons in most metals, 10^4 to 10^5 degrees, which render only the degenerate state accessible for experimenting. There is, however, one substance in which, owing to certain special conditions, both these difficulties are eliminated. I mean the crystal of graphite.

Graphite is a hexagonal crystal with a perfect basal cleavage. The carbon atoms in it are arranged in layers parallel to the basal plane, the atoms in each layer forming a regular hexagonal network. The binding between neighbouring layers is extremely loose, and is probably of the van der Waals type, as is evidenced by the very large distance of separation between them, viz. 3.4 A.U., as compared with the distance of 1.42 A.U. between adjacent atoms in the same layer. Three of the electrons in each carbon atom will be utilized in binding it to its three neighbours in the basal plane, and the fourth will be practically free to migrate from atom to atom in the basal plane, much in the same manner as the free electrons in a metal. The probability of the electron jumping to the next layer will be very small.

The conditions obtaining in graphite are very favourable for a verification of the Landau diamagnetism. With a magnetic field incident along the hexagonal axis, we are concerned with the motions of the electrons in the basal plane only, and these motions, as we have seen, are free; the diamagnetic properties of the medium will therefore be similar to those of a free-electron gas. The restriction of the freedom of the electrons practically to the basal plane actually proves to be an advantage; the restriction will be equivalent to an enormously increased effective mass for the electron for motion along the normal to the plane, and as a result the spacing of the energy levels along this direction will become much narrower, and hence the degeneracy temperature much smaller, than for electrons that are free to move in all directions. Lastly, the spin-moments of the electrons in graphite are paired in such a manner as to give zero paramagnetism.

Experimentally, graphite crystal does have an abnormal diamagnetism, which is confined to the direction of the hexagonal axis (the susceptibility in the basal plane being practically the same as that of diamond), and which conforms to the Curie law (4) at high temperatures, and to the temperature-independent value (5) at low temperatures, with the *number of free electrons n equal to one per carbon atom and the degeneracy temperature $T_0 = 520^\circ\text{K}$* . At all temperatures (in the range investigated) the diamagnetism per carbon atom is found to be the same as the Landau diamagnetism per electron of a free-electron gas having a degeneracy temperature of 520°K . The theoretical values for the specific susceptibility (per gm.) of graphite

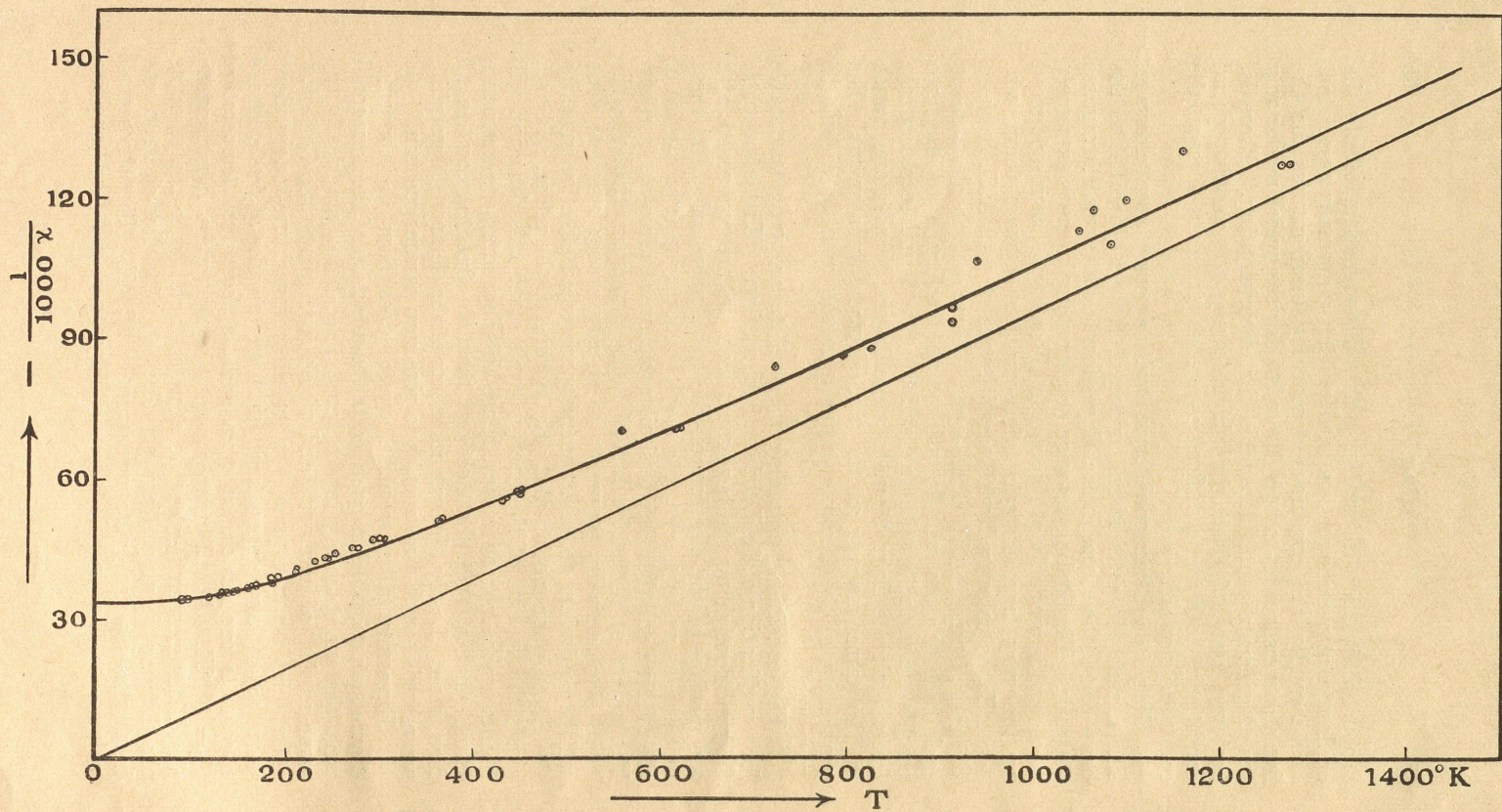


FIG. 2. Temperature variation of the magnetic anisotropy of graphite.

calculated on this basis are represented by the curve drawn in Fig. 2. The straight line which the curve tends to reach asymptotically at high temperatures, namely that corresponding to the Curie law (4), is also drawn in the figure. The circles denote the experimental values obtained by Mr. Ganguli and the present writer, and it will be seen that they all lie close to the theoretical curve.

That one electron per carbon atom should be free to move about in the basal plane agrees, as we have just seen, with the known structure of the crystal. It is further gratifying to find that there is a Brillouin zone which can just accommodate 3 electrons per carbon atom, which is a flat hexagonal prism bounded by $\{000,2\}$ and $\{2\bar{1}\bar{1},0\}$, and the energy-discontinuities across all the faces of the zone are large. There is a bigger zone bounded by $\{000,2\}$ and $\{2\bar{2}0,0\}$ which can just contain all the 4 valency electrons, but the energy-discontinuity across $\{2\bar{2}0,0\}$ is small.

The restriction of the freedom of motion of the metallic electrons in graphite to the basal plane is also evidenced by the enormously greater electrical conductivity of the crystal in the basal plane than along the normal to the plane; the ratio of the two conductivities, according to some recent measurements by Mr. Ganguli and the present writer, is larger than 10^4 , probably very much larger.

The agreement between the experimental and the theoretical values plotted in Fig. 2 may be regarded as an experimental demonstration of the Landau diamagnetism of a free-electron gas, and of its temperature variation in accordance with the statistics of Fermi and Dirac.

THE MOBILE ELECTRONS IN AROMATIC MOLECULES

Further, the magnetic data for graphite lend support to the view that one electron per carbon atom in the crystal is practically free to migrate from atom to atom through the whole layer. Following Lennard-Jones we shall call it the mobile electron, so as to distinguish it from the other three valency electrons in each carbon atom, which are localized and take part in binding it to its three neighbours. The occurrence of such mobile electrons is characteristic of all aromatic molecules—each layer in graphite can be regarded as a single molecule consisting of a very large number of condensed benzene rings—and is an essential feature of the quantum mechanical theories of the structures of these molecules. Their mobility is a necessary consequence of the Uncertainty Principle, according to which the larger the region assigned to these electrons, the smaller would be their kinetic energy. Any localization of these mobile electrons, such as is implied, for example, in the conventional

double-bond (in which a pair of such electrons is involved), will naturally correspond to a very large kinetic energy for these electrons; it is equivalent to restricting the wave-lengths of the standing electron waves to small values of the order of the length of the double-bond, whereas if the electrons are mobile, greater wave-lengths, of the order of the dimensions of the whole molecule, will also be permitted, thus conducing to a lowering of the energy, and to a correspondingly increased stability.

This is essentially the solution offered by quantum mechanics to the old controversy regarding the locations of the extra bonds in the benzene ring: they are not located at all! If we prefer it, we may, following Pauling and Wheland, express the same result in this form: the actual structure of the benzene ring is that obtained by the 'resonance' between the following

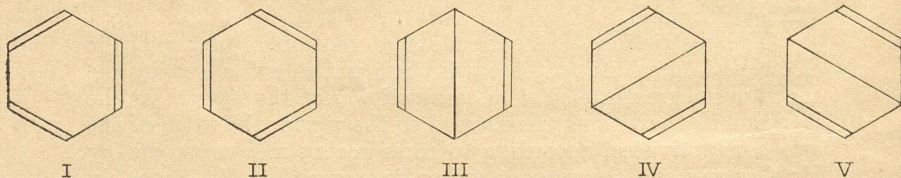


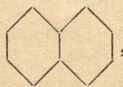
FIG. 3.


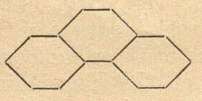
five canonical structures, the coefficients to be attached to the wave-functions representing these structures being given by

$$\psi = 0.622 (\psi_I + \psi_{II}) + 0.271 (\psi_{III} + \psi_{IV} + \psi_V).$$

The first and the second of these structures can be recognized as Kekulé's and the remaining three as Dewar's. The structures proposed by Claus, Ladenburg and others, can all be obtained from the above five by suitable combinations.

The number of such canonical structures becomes very large even for the simplest of condensed ring molecules. For

example for naphthalene , the number of such structures is 42, and for the three-ringed molecules anthracene

 and phenanthrene , the number

is 429, and so on. If one has a partiality for any particular model, he can with a little diligence find his favourite in this list.

THE DIAMAGNETISM OF THE MOBILE ELECTRONS

One direct consequence of the freedom of the mobile electrons in benzene to migrate from atom to atom over the whole ring, would be an abnormal diamagnetism, confined to the direction perpendicular to the plane of the ring, because the diamagnetic moment is proportional to the area of the orbits described by the electrons under the influence of the magnetic field, and the mobile electrons can describe very much larger orbits in the plane of the benzene ring than the localized electrons. These diamagnetic effects should be even more marked in plane condensed ring molecules like naphthalene, anthracene, etc., in which the migrations of the mobile electrons can be more extensive. This explains the remarkable diamagnetic anisotropy exhibited by aromatic molecules. For example in benzene, the diamagnetic susceptibility along the normal to the plane of the molecule is nearly $2\frac{1}{2}$ times that along directions in the plane. Indeed the observed large diamagnetic anisotropies of these molecules offer the most striking evidence for the presence of the mobile electrons.

When such magnetically anisotropic molecules are arranged in a regular manner as in a crystal—in most organic crystals the molecules retain their individuality—the crystal as a whole will naturally exhibit an anisotropy, whose magnitude will depend on the anisotropy of the individual molecules and on their orientations relatively to one another. The closeness of approach of the molecules, which may not be the same along different directions in the crystal, will have practically no effect on the crystal anisotropy, since the diamagnetic moments induced in them will be too feeble to influence one another. In other words, the susceptibility of the crystal along any given direction will be merely the sum of the susceptibilities along this direction of all the constituent molecules.

When the magnetic constants of the molecule are already known, from measurements of the magnetic double-refraction of the substance in the liquid state or in state of solution in suitable solvents, magnetic studies on the crystal should enable us, in favourable cases, to obtain useful information about the orientations of the molecules in the crystal lattice. Such information will be very helpful in any structural analysis of the crystal by X-ray methods, since it may save much labour in the preliminary analysis, and will in any case offer an independent check on some of the results of the X-ray analysis.

I shall not deal further with this aspect of the magnetic studies on single crystals, and I shall now take up the converse aspect, namely that when the molecular orientations are already known from detailed X-ray studies, the crystal data enable us to calculate the principal magnetic constants of the molecules, which interest us here. This is a more direct, and more

accurate method for calculating the molecular magnetic constants, than the one based on measurements of the magnetic double-refraction in the liquid state, and besides is more general in its applicability.

THE MAGNETIC ANISOTROPIES OF SOME PLANE AROMATIC MOLECULES

Extensive measurements have been made by Bhagavantam, Banerjee, Mrs. Lonsdale and the present writer on the magnetic properties of organic crystals, particularly of the aromatic class. For some of these crystals complete X-ray analyses have been made by Robertson and others, by the Fourier method. I give in the following Table the magnetic constants for some plane aromatic molecules, calculated from these data. K_1 , K_2 and K_3 represent the three principal diamagnetic susceptibilities of the molecule, per gm. mol., and are expressed in the usual unit 10^{-6} c.g.s. e.m.u.; K_3 refers to the direction normal to the plane of the molecule; the directions of K_1 and K_2 in the plane of the molecule are as marked at the head of the Table. In those crystals in which the X-ray data are not sufficiently precise to enable us to calculate K_1 and K_2 separately, only one value is given in the Table, which will be a good approximation to either of them.

It will be seen from the Table that for all the molecules, the susceptibility along the normal to the molecular plane, namely K_3 , is numerically much larger than either K_1 or K_2 , in the plane, and that K_1 and K_2 are of comparable magnitudes. The difference, $\Delta K = K_3 - \frac{1}{2}(K_1 + K_2)$, which may be taken to be the contribution from the mobile electrons, wholly directed along the K_3 axis, is given in the last column of the Table; it is roughly proportional to the number of benzene rings in the molecule.

OPTICAL EVIDENCE FOR THE MOBILE ELECTRONS IN AROMATIC MOLECULES

The restriction of the freedom of migration of the mobile electrons in these molecules to the molecular plane, is also evidenced by the striking directional variations in some of the optical properties of these molecules, observed some time ago by Mr. P. K. Seshan and the present writer. Let us take for example the plane condensed ring compounds naphthacene

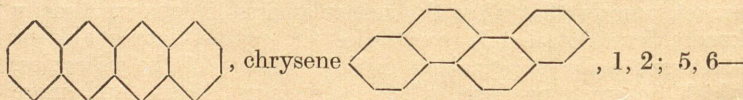
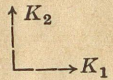

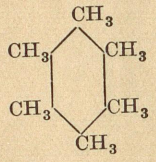
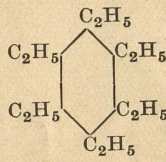
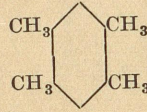
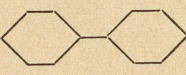

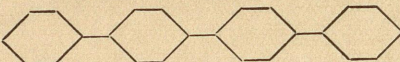
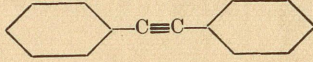
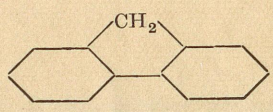
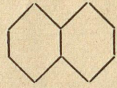

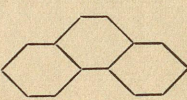
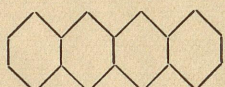
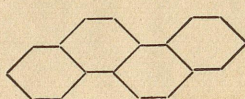
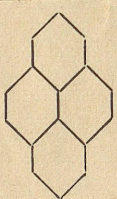
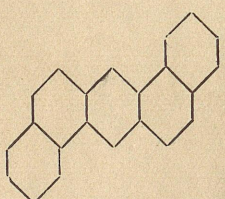
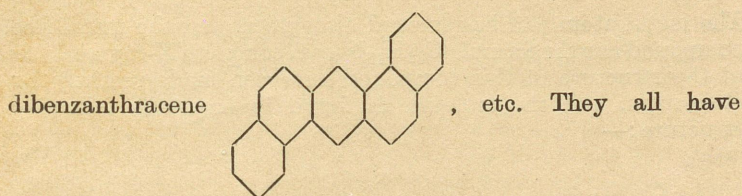


TABLE I

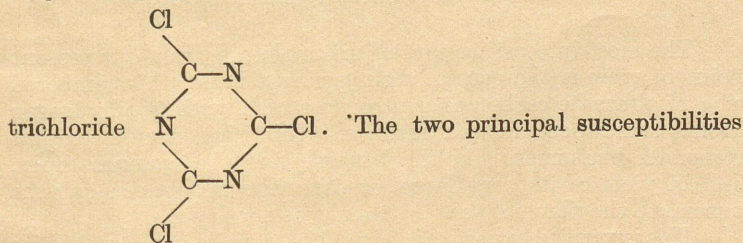
Molecule		$-K_1$	$-K_2$	$-K_3$	$-\Delta K = \frac{1}{2}(K_1 + K_2) - K_3$
Benzene		37	37	91	54
Hexamethylbenzene		102	102	164	62
Hexaethylbenzene		165	165	231	66
Durene		82	77	144	65
Diphenyl		63		182	119
Terphenyl		97	88	271	178
Quaterphenyl		122	110	372	256
Tolane		80	67	197	123
Fluorene		73		194	121
Naphthalene		56	54	169	114
Anthracene		76	63	252	183
Phenanthrene		74		240	166
Naphthacene		93		295	202
Chrysene		88	83	311	226
Pyrene		81		303	222
1, 2; 5, 6-Dibenzanthracene		110		358	248



characteristic absorption and fluorescence bands in the visible region of the spectrum, which are presumably due to the transitions of the mobile electrons. It is found experimentally that it is only the component in the molecular plane of the electric vector of the incident light-wave, which is absorbed by the molecule, whereas the component along the normal to the plane is not absorbed at all. In fluorescence also it is the component of the electric vector parallel to the molecular plane which excites fluorescence, the perpendicular component being quite inactive. An elegant quantum mechanical interpretation of these properties has recently been published by F. London.

OTHER CONJUGATED SYSTEMS

Besides the benzene ring there are other plane ring structures which, on the conventional view, have alternate single and double bonds. Their diamagnetic properties should be very similar to those of the benzene ring, since they also must have mobile electrons which can migrate all over the ring. I shall mention here two such compounds, studied recently for their magnetic properties by Mrs. Lonsdale. One is cyanuric



of this molecule in the plane of the cyanuric ring are -70.9 and -71.2 respectively, whereas the third susceptibility, which is along the normal to the ring, is -101.3 , which is numerically much larger. The diamagnetic contribution from the mobile electrons is thus about -40 , as compared with the value -54 of the mobile electrons in the benzene ring.

The second compound is metal-free phthalocyanine. The phthalocyanines are complex organic compounds, which are related to the natural porphyrins. They have been studied extensively by Linstead and his collaborators, and they have the formula $C_{32}H_{16}N_8M$, where M is a metal atom like Ni , Cu , etc.

The metal atom can be removed altogether, and the metal-free compound has the formula $C_{32}H_{18}N_8$. A complete X-ray analysis of the structure of this compound has been made recently by Robertson, and the molecule is found to have the following structure:—

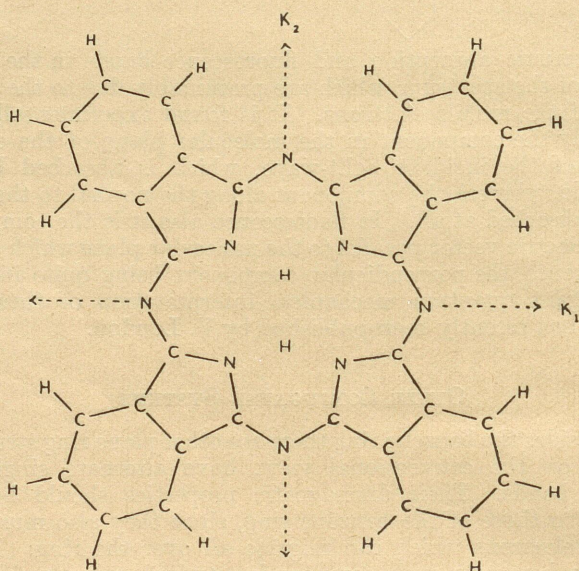


FIG. 4. Metal-free phthalocyanine molecule.

The most interesting part of this molecule, from our present point of view is the central zig-zag ring. It is a 16-membered ring of alternate carbon and nitrogen atoms, with two hydrogen atoms somewhere in the interior. This ring should exhibit resonance phenomena like the benzene and the cyanuric rings, and in view of its very large size, its diamagnetism along the normal to the plane of the ring should be enormous.

This is verified experimentally. The principal susceptibilities of the molecule are $K_1 = -120$, $K_2 = -165$, $K_3 = -982$. The susceptibility along the normal to the molecular plane is thus nearly 7 times that for directions in the plane. Even after allowing for the contributions from the outer rings, the contribution from the central 16-membered ring should be very large indeed, reminding one of the magnitudes involved in graphite.

SOME THEORETICAL CONSIDERATIONS

Attempts have been made to calculate theoretically the magnitude of the diamagnetic anisotropy in some simple aromatic

molecules. Adopting a semi-classical theory—which we have adopted here in our description of the diamagnetic properties of the aromatic molecules—Pauling and Mrs. Lonsdale have evaluated the effective sizes of the orbits which the mobile electrons will describe in the plane of the molecule under the influence of a magnetic field incident perpendicular to the plane, and thence have calculated the contributions which these electrons will make to the diamagnetism. The values thus obtained agree roughly with the experimental values.

On this basis, for example, the large anisotropy of graphite would be attributed to the very large size of the orbits which the mobile electrons can describe in the basal plane, in the magnetic field. On this view any temperature-variation of the susceptibility is not contemplated, and indeed will be difficult to explain. But we found that experimentally the temperature-variation of the susceptibility is very marked in graphite, and also that this variation can be explained quantitatively on the quantum mechanical theory, as due to the change of the energy distribution of the electrons with temperature. To explain satisfactorily the diamagnetic behaviour of the mobile electrons in the aromatic molecules one has to adopt a similar method.

A quantum mechanical theory has been developed recently by F. London, and he has calculated the anisotropies of some simple aromatic molecules in terms of the anisotropy of the benzene molecule. His theoretical values are given in the following Table along with the experimental values for comparison:—

TABLE II

Molecule	$\frac{\Delta K}{\Delta K_{\text{benzene}}}$	
	Theoretical	Experimental
Naphthalene	2.19	2.11
Anthracene	3.45	3.39
Phenanthrene	3.19	3.07
Pyrene	4.46	4.11
Diphenyl	2.21	2.20

Attention may be drawn to one or two features in the experimental values, which are not obvious on Pauling's theory, but which follow from London's calculation: the anisotropy of diphenyl is found to be considerably larger than twice that of benzene; and there is a marked difference between the anisotropies of anthracene and phenanthrene.

It is interesting that experimentally the diamagnetic susceptibilities of the mobile electrons in chrysene, pyrene, and other condensed ring compounds do show an appreciable

temperature-variation. This variation, however, is much smaller than in graphite, suggesting that the kinetic energies of the mobile electrons in these molecules should be much larger than in graphite. This is indeed to be expected.
