

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. From the application of quantum mechanics, and detailed investigations on the Raman and infra-red spectra of benzene and its deuterio-isomers, it is found 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. These mobile electrons have interesting magnetic properties, not dissimilar to that of free electrons in metals.

Many properties of metals 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. These electrons can be regarded as forming a free-electron gas but their spin-susceptibility is limited by the degeneracy prevailing at all ordinary temperatures, and is given by $k\beta = 3/2 \frac{n\mu^2}{kT_0}$, where T_0

the degeneracy temperature $= \frac{h^2}{8mk} \left(\frac{3n}{\pi} \right)^{2/3}$.

Contrary to the classical theory, the free-electron gas can also exhibit a diamagnetism, as shown by Landau, of value equal to $\frac{-n\mu^2}{2kT_0}$ (when $T \ll T_0$). It is difficult to verify this Landau's diamagnetism particularly on account of the predominant paramagnetism with which it is normally associated. In the case of graphite, however, conditions are favourable for such a verification, as here the spin moments of the electrons are paired to give zero paramagnetism and the restriction of motion of electrons practically to the basal plane has effectively lowered the degeneracy temperature to 520° K. Experimental values beautifully confirm Landau's theory with one electron per carbon atom free to move about in the basal plane.

The occurrence of such mobile electrons is characteristic of all aromatic molecules 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. The actual structure of the aromatic rings is that obtained by "resonance" between a number of canonical structures. An important consequence of the freedom of the mobile electrons to move

from atom to atom over whole rings, as in benzene, naphthalene, etc., is the abnormal diamagnetism perpendicular to the plane of the ring.

When these magnetically anisotropic molecules are arranged in a regular manner as in a crystal, the crystal as a whole will naturally exhibit an anisotropy, whose magnitude will depend upon the anisotropy of the individual molecules and on their orientations relative to one another. Where the magnetic constants of the molecule are already known, magnetic studies on the whole crystal enable us in favourable cases to obtain useful information about the orientations of the molecules in the crystal lattice. Conversely, when molecular orientations are already known from detailed X-ray studies, the principal magnetic constants of the molecules can be calculated with high accuracy. Such calculations for a large number of aromatic molecules show that the diamagnetic contribution due to the mobile electrons is roughly proportional to the number of benzene rings in the molecule. Other conjugated molecules with plane ring structures such as cyanuric trichloride and phthalocyanines also show diamagnetic anisotropy, and sometimes, as in the case of phthalocyanines with a 16-membered ring, the susceptibility normal to the plane is 7 times that for the direction in the plane.

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. Thus in naphthalene, chrysene, etc., it is only the component of the electric vector of the incident light wave in the molecular plane which is absorbed by the molecule, whereas the component along the normal to the plane is not absorbed.

Pauling has evaluated, adopting a semi-classical theory, the effective size of orbits which the mobile electrons will describe in the plane of the molecule under the influence of a magnetic field perpendicular to the plane and thence the diamagnetic susceptibility. On this view any temperature variation in susceptibility such as is markedly observed in graphite, cannot be explained. This temperature coefficient can however be accounted for quantitatively on the quantum mechanical theory, as due to the change in the energy distribution of the electrons with temperature. According to a theory more recently developed by London, other features such as that the anisotropy of diphenyl is larger than twice that of benzene, are also accounted for.

* Summary of Presidential Address,—by Prof. K. S. Krishnan, D.Sc. Physics Section—Indian Science Congress, Madras, 1940.