

Magnetic Anisotropy and Electronic Structure of Aromatic Molecules

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In a recent paper Pauling (1936) calculates the diamagnetic anisotropy of benzene and other aromatic hydrocarbon molecules on "the assumption that the $2p_z$ electrons are free to move under the influence of the impressed fields from carbon atom to adjacent carbon atom". He points out that this is a quantitative extension of previous and generally accepted explanations of magnetic anisotropy given by Ehrenfest (1925, 1929) for Bi and Sb, and by Raman and Krishnan (1927) and Raman (1929*a, b*) for benzene and its derivatives. The idea that certain electrons can move in this way is implicit in the theory of molecular orbitals, as applied by Hückel (1931*a, b*, 1932, 1933) to aromatic and unsaturated molecules. Hückel (1934), in fact, pointed out that the application of the theory to such problems as magnetism and light absorption would be a task for further research.

With the object of applying the theory of molecular orbitals to the quantitative explanation of diamagnetic anisotropy, I have for some time been engaged on a determination of the diamagnetic constants of substances which can be used for this purpose, including some which had been previously examined and which then gave the results used by Pauling (Krishnan, Guha and Banerjee 1933; Krishnan and Banerjee 1935). It was clear, almost from the first, that the original measurements on naphthalene and anthracene were out of harmony with the rest; these measurements were repeated independently by Krishnan and myself, and corrected results were published in a joint paper (Lonsdale and Krishnan 1936). These new results remove a difficulty commented upon by Pauling. I have also determined the diamagnetic constants of certain new compounds, especially cyanuric triazide, cyanuric trichloride and metal-free phthalocyanine. This work was begun and completed and the following paper written, in ignorance that Pauling was making the calculations described in his recent paper, and it therefore adds independent evidence in favour of the essential principle.

Measurements of magnetic anisotropy of crystals of low symmetry, together with an exact determination of their internal structure, may be

used to calculate the magnetic anisotropy of single molecules (Krishnan and Banerjee 1935; Lonsdale and Krishnan 1936). It is invariably found that the diamagnetic susceptibility of aromatic molecules is numerically much greater in a direction normal to the plane of the molecule (such molecules generally being plane or nearly plane configurations of atoms) than in the directions parallel to the molecular plane. In spite of this remarkable anisotropy, the mean susceptibility is additive to a good degree of approximation except in the case of condensed molecules, for which special correcting factors must be taken into account. That such an additive law holds has been well known since the classic researches of Pascal (1910, 1912, 1913) who, however, knew nothing of the magnetic anisotropy which is such a striking feature of aromatic molecules.

It has also been realized for some time that by applying the Larmor-Langevin formula

$$\chi_A = -\frac{Ne^2}{6mc^2} \sum_n \bar{r}_i^2$$

to atoms in *aliphatic* compounds a very good estimate of the atomic diameter, agreeing with that given by X-ray and other methods, is obtained. The formula of course only applies to spherically symmetrical atoms; quantum mechanical treatment (van Vleck 1932) shows that it must be modified for many-electron systems and also for molecules, to allow for the mutual interaction of electrons and nuclei. In other words, the electrons in such systems are not completely free to precess under the influence of the magnetic field. In fact, however, the successful applications of the formula, as well as the additivity of other physical properties such as refractivity, show that in *aliphatic* compounds the atoms do behave in many respects as if they were free and spherically symmetrical.

Examples: The diamagnetic susceptibility of diamond is

$$-5.9 \times 10^{-6} \text{ c.g.s. e.m.u./g.-atom.}$$

The contribution of the atom core may be taken as about equal to that of the C^{+4} ion, estimated by Pauling (1927) to be -0.15×10^{-6} . Hence the diamagnetism due to the four valency electrons alone is -5.75×10^{-6} . Applying the formula

$$-5.75 \times 10^{-6} = -2.832 \cdot 10^{10} \sum_4 \bar{r}_i^2$$

$$\sqrt{\bar{r}_i^2} = 0.71 \text{ \AA}$$

as compared with 0.77 \AA, the value of the "effective atomic radius" obtained from X-ray analysis.

For chlorine, Pascal found $\chi_A = -20.1 \times 10^{-6}$. The atom-core diamagnetism will be nearly equal to that of Cl^{+7} , given by Pauling (1927) as -1.2×10^{-6} , and the main contribution to the atomic susceptibility must therefore be due to the increased energy of the seven valency electrons in the magnetic field,

$$-(20.1 - 1.2) \times 10^{-6} = -2.832 \times 10^{10} \times 7(\overline{r_i^2}),$$

$$\sqrt{\overline{r_i^2}} = 0.98 \text{ \AA}.$$

From X-ray and electron diffraction data, the effective atomic radius of chlorine is 0.99 \AA.

Other convincing evidence of the applicability of the Larmor-Langevin formula is recorded by Bhatnagar and Mathur (1935).

AROMATIC (BENZENE) COMPOUNDS

If the Larmor-Langevin formula is applied to atoms in *aromatic* molecules, however, the mean radii obtained are not at all the same as those given, for example, by Fourier analysis of electron density in the crystal. This is to be expected, for the very anisotropy shows that the atoms are certainly no longer spherically symmetrical, and that precession of the electron orbits will therefore be opposed by an anisotropic field of force. If the mean atomic susceptibility χ_A be taken as the same for carbon atoms in both aliphatic and aromatic compounds, the correcting factor λ in Pascal's formula

$$\chi_M = \Sigma \alpha \chi_A + \lambda$$

is comparatively large for aromatic compounds, and increases as the molecules become more condensed, being overwhelmingly large for crystalline graphite.

It is worth while, however, to consider whether the problem of the aromatic molecule can be treated quantitatively as that of a system of spherically symmetrical atoms, to which the Langevin formula may be applied without correction, together with a system of electrons constrained to precess only in non-spherical orbits. This is reasonable, for the peculiar "aromatic" properties of such molecules as benzene, naphthalene, pyrene, etc., appear to be due entirely to the π electrons,* which have antisymmetrical eigenfunctions with respect to the plane of the molecule. These π electrons are unaccounted for by ordinary valency considerations and

* Following E. Hückel: the π electrons are equivalent to Pauling's p_z electrons.

the earlier benzene formulae were simply different ways of representing their possible fields of action.

Quantum-mechanical treatment of complex molecules is necessarily in the experimental stage. The conception underlying the method of molecular orbitals, already applied by E. Hückel (1934) to aromatic and unsaturated molecules, is one that leads to reasonable results when applied to calculations based on magnetic anisotropy. The eigenfunction of the π electrons is assumed to extend over the whole of the space occupied by the molecule, but for practical purposes we shall take the molecular orbit of the π electron to be plane (not necessarily circular) and in the plane of the atomic nuclei.

Thus in the case of benzene, naphthalene, etc., we suppose that three of the valency (s) electrons of each aromatic carbon atom are perfectly normal, that they occupy spherically symmetrical orbits, are perfectly free to precess and contribute equally in all directions to the diamagnetic susceptibility. The fourth (π) electron occupies a plane orbit (or an annular ring orbit) which is free to precess only in its own plane, that is, in the plane of the atomic nuclei, and it therefore contributes nothing to the susceptibilities *in* the molecular plane. The electron formally attached to the hydrogen atom is also assumed to occupy a spherically symmetrical orbit. In each CH group, therefore, there are four s electrons for which free precession is assumed and one π electron for which precession in one plane only is allowable. The diamagnetism due to the atom core (-0.15×10^{-6} for C^{+4}) may be neglected, compared with that due to the valency electrons. It follows that the excess of diamagnetism in the direction normal to the plane of the molecule is due solely to, and is the entire contribution of, the precession of the π -electron orbits.

Since the π -electron orbits precess only in one plane, the formula to be applied to the calculation of the π -orbital area is

$$\Delta K_M = -\frac{Ne^2}{4mc^2} \sum_p \bar{r}_k^2,$$





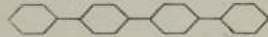
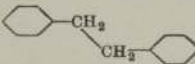
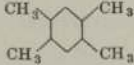
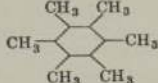

where p is the number of π electrons in the molecule, r_k the radius of a circular orbit of equivalent mean area in the plane in which precession is permitted, ΔK_M is the excess of K_{\perp} , the molecular susceptibility normal to that plane, over K_{\parallel} , the molecular susceptibility in that plane. In practice K_{\parallel} is taken as the mean of the two susceptibilities in the plane of the molecule, these being generally not quite equal. The formula

$$(K_{\parallel})_M = -\frac{Ne^2}{6mc^2} \sum_n \bar{r}_i^2$$

gives the mean square radius of the spherically symmetrical orbits of the n normal valency electrons (counted on a basis of four to each aliphatic carbon atom, three to each aromatic carbon atom, one to each hydrogen atom).

The values of the molecular susceptibilities have been determined with some accuracy for a number of simple aromatic compounds (Lonsdale and Krishnan 1936) and in Table I are listed the corresponding values of

TABLE I





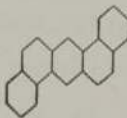
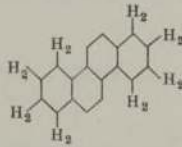
Name and formula	Mean $-K$ $\times 10^6$	Calc. (*)	Valency electrons			π electrons		
			$-K_{\parallel}$ $\times 10^6$	n	$\sqrt{r_i^2}$	ΔK_M	p	$\sqrt{r_k^2}$
Naphthalene 	93.0	85.2	55.0	38	0.71	114.0	10	1.64
Anthracene 	130.1	115.8	69.2	52	0.69	182.6	14	1.75
Chrysenes 	160.7	144.4	85.7	66	0.68	225.2	18	1.72
<i>p</i> -Diphenylbenzene 	152.1	152.2	92.5	68	0.70	178.8	18	1.52
<i>p</i> -Diphenylbiphenyl 	201.3	201.0	116	90	0.68	256	24	1.57
Dibenzyl 	127.7	127.0	88.7	58	0.74	116.8	12	1.51
Durene 	101.2	102.8	79.9	48	0.77	61.5	6	1.55
Hexamethylbenzene 	122.5	125.4	102.0	60	0.78	61.9	6	1.56
<i>p</i> -Benzoquinone 	40.0	—	—	—	—	40.6	4	1.55

* Calculated from additivity data: $\begin{cases} K_{\text{aromatic carbon}} = -6.2 \times 10^{-6}, \\ K_{\text{aliphatic carbon}} = -6.0 \times 10^{-6}, \\ K_{\text{hydrogen}} = -2.9 \times 10^{-6}. \end{cases}$

Note—These additivity data apply to mean susceptibilities, not to K_{\parallel} , for which however, $K_{\text{aliph.C}}$ and K_{H} should be unaltered. The above values of $K_{\text{aliph.C}}$ and K_{H} (in combination with C) are derived from series of measurements on various aliphatic long-chain compounds; see Bhatnagar and Mathur (1935, p. 73). The departure from the additivity rule for condensed compounds is most marked.

$\sqrt{r_i^2}$ and $\sqrt{r_k^2}$ respectively. Similar values are given in Table II for aromatic compounds the molecular susceptibilities of which are less accurately, but still approximately, known; they have been estimated from the rule, referred to by Lonsdale and Krishnan (1936), that for simple aromatic molecules the minimum (numerical) susceptibility in the (010) plane of monoclinic crystals is approximately equal to K_{\parallel} , the molecular susceptibility in the plane of the benzene nuclei. The tables also contain some compounds for which ΔK_M alone is accurately known, or for which K_{\parallel}

TABLE II

Name and formula	Mean $-K$ $\times 10^6$	Calc. as before	Valency electrons			π electrons		
			$-K_{\parallel}$ $\times 10^6$	n	$\sqrt{r_i^2}$	ΔK_M	p	$\sqrt{r_k^2}$
Benzene  (i)	55.1	54.6	37.3	24	0.74	54.0	6	1.46
	(ii)		53.1			32.5		61.9
Diphenyl 	102.9	103.4	63.4	46	0.70	118.6	12	1.53
Phenanthrene 	129	115.8	74	52	0.71	166	14	1.67
Pyrene 	154.9	128.2	80.6	58	0.70	232.9	16	1.86
Dibenzanthracene 	193	177	110	80	0.70	248	22	1.63
Hexaethylbenzene $C_6(C_2H_5)_6$	187	196	165	96	0.78	66	6	1.61
Hexachlorbenzene C_6Cl_6	145.6	—	—	—	—	65.3	6	1.59
Octahydro- chrysene 	—	—	—	—	—	109.6	10	1.61
Graphite:								
(1) Crystalline	136	6.2	6.0—	3	0.84—	~258		7.80
(2) Spectroscopic carbon	7.6		4.8	6	0.75	approx. ~5	1	1.37

(i) Data given by Krishnan and others (1933). The method used for computing the anisotropy was an indirect one.

(ii) Mean susceptibility measured by Cabrera and Fahlenbrach (1934). Anisotropy calculated by analogy with $C_6(CH_3)_6$, assuming contribution of (CH_3-H) to be symmetrical in all directions.

includes contributions from atoms other than C and H. The atom-core diamagnetism has been neglected; if allowed for it would lower the values of $\sqrt{r_i^2}$ by about 1 %.

It appears from these calculations that the average effective radius of the normal valency electrons in benzene derivatives is about 0.70 Å, increasing to 0.78 Å as the number of aliphatic carbon atoms and hydrogen atoms in the molecule increases. The atomic susceptibility of hydrogen (in combination with carbon)* is about -2.9×10^{-6} , which would indicate an atomic radius of about 1 Å, and though this value may vary with the conditions of combination, since the additive constants are undoubtedly somewhat elastic, yet it is probable that the presence of many hydrogen atoms is even more effective than that of aliphatic carbon atoms in raising the average orbital radius. The values found may be compared with the effective atomic radii as given by Fourier analysis of crystal structures and electron diffraction of vapours.

$r = 0.69_5$ Å for aromatic carbon, increasing to 0.71 Å for highly condensed derivatives,

$r = 0.77$ Å for aliphatic carbon.

The experimental data for K_{\parallel} for graphite is only approximate, so that the deduced radius $0.84 \rightarrow 0.75$ may be considered as in satisfactory agreement with the other results.

On turning to a consideration of the π electrons, the striking fact emerges that, in mono-nuclear compounds (which best obey a simple additivity rule) the average effective radius of the π -electron orbits is 1.50–1.60 Å, which may be compared with 1.39 Å, the radius of the benzene nucleus itself. In the condensed ring compounds (which are more diamagnetic than would be expected from a strict additivity rule) the average orbital area of the π electrons is greater, but it is not equal to the area of the whole condensed nucleus. It seems likely, therefore, that for such compounds a large proportion of the π electrons (or each π electron for a large proportion of the time) occupy orbits equal in area to a single benzene ring, only a few occupying larger orbits.

The most compact arrangement of benzene nuclei is, of course, to be found in graphite, for which the anisotropy is so very large that it leads to

* Pauling uses the value $K_{\text{H}} = -2.0 \times 10^{-6}$, half the value of the susceptibility of molecular hydrogen. It may be pointed out, however, that the mean value of $\chi_{\text{CH}_2} = -11.85 \times 10^{-6}$, derived from a large number of compounds, including aromatic compounds, definitely leads to the higher value. Pauling's data would give $\chi_{\text{CH}_2} = -(6.0 + 4.0) = -10.0$.

an average π -orbital radius of 7.80 Å, the average area being therefore equal to that of about 30 benzene nuclei.* According to Ganguli (1936) the anisotropy of spectroscopic carbon, which is graphite in a fine state of division, is no greater than that of benzene (Table II). The actual measurements are, however, only approximate.

Other interesting points arise out of the tables. Double bonds in any molecule tend to show their presence by a small anisotropy in the magnetic susceptibilities, and there is in the plane of the *p*-benzoquinone molecule an anisotropy ($K_1 = -24.3$, $K_2 = -28.7$) which may possibly be traced to the C=O bonds. The anisotropy in the third direction, ($K_3 = -67.1$), is however, too large to be attributed to the presence of double bonds alone, and is, in fact, equivalent to that due to four π electrons. It seems, therefore, that the magnetic evidence is definitely against the fixation of double bonds in the benzoquinone nucleus, at least when the molecule is in a strong magnetic field of force. In octahydrochrysene the reduced rings appear to contribute nothing to the anisotropy, which is equivalent to that of the naphthalene nucleus alone, as might be expected.

CYANURIC COMPOUNDS

A study of the magnetic susceptibilities of some *cyanuric* compounds has shown that these substances, which have many aromatic properties, are also strongly anisotropic, though less so than benzene or its derivatives. For cyanuric triazide, $C_3N_3(N_3)_3$, the molecule of which is plane and symmetrical about a three-fold axis (Knaggs 1935), $\Delta K_M = -21.8 \times 10^{-6}$, the numerically larger diamagnetic susceptibility being, as in benzene derivatives, normal to the molecular plane. For cyanuric trichloride (Lonsdale 1936), $C_3N_3Cl_3$, $\Delta K_M = -31.3 \times 10^{-6}$. In each of these compounds there are six electrons unaccounted for by ordinary valency considerations. If these six electrons occupy molecular orbits of approximately the same area as that of the cyanuric nucleus itself, the anisotropy should be almost twice as much as is experimentally found. On the other hand, if the electrons are definitely paired, forming double bonds, very little anisotropy should exist. It follows from the experimental data that the π electrons do occupy molecular orbits, but with a strong tendency to the fixation of double bonds in the nucleus; one may say that there is an alternation of electron density round the nucleus, but not as great as would be expected for alternate double and single bonds between C and N atoms. In cyanuric triazide

* Pauling estimates the *maximum* orbital radius to be about 20 Å.

Miss Knaggs did in fact find an alternation of C to N distances in the cyanuric nucleus. This alternation should be somewhat less marked for cyanuric trichloride.

METAL-FREE PHTHALOCYANINE

Preliminary measurements have recently been made on the magnetic anisotropy of metal-free phthalocyanine, the crystal structure of which is accurately known by X-ray analysis (Robertson 1936). The anisotropy of this compound is nearly fifteen times as great as that of benzene. The crystals are lath-shaped (monoclinic, with b along the length and (001) as the tabular face of the lath) and the biggest weigh about 0.1 mg. Absolute measurements of the susceptibility have not yet been made, but the anisotropy has been measured in two directions by Krishnan's second method (Krishnan and Banerjee 1935). The crystal was first suspended with its length (b -axis) vertical and it was found that the larger numerical susceptibility χ_2 in the (010) plane made an angle of $15\frac{1}{2}^\circ$ with the (001) plane in the acute angle β . [In Krishnan's notation, $\theta = -15\frac{1}{2}^\circ$, $\beta = 122^\circ$, hence $\psi = 47\frac{1}{2}^\circ$.] The mean of measurements on several crystals gave

$$\chi_2 - \chi_1 = -372 \times 10^{-6} \pm 5 \%$$

On suspending the crystal with its a -axis vertical it was found that $\Delta\chi = -370 \times 10^{-6} \pm 10 \%$,

$$\begin{aligned} \Delta\chi &= \chi_3 - (\chi_1 \cos^2 15\frac{1}{2} + \chi_2 \sin^2 15\frac{1}{2}) \\ &= (\chi_3 - \chi_1) - (\chi_2 - \chi_1) \sin^2 15\frac{1}{2}, \end{aligned}$$

whence

$$\chi_3 - \chi_1 = -397 \times 10^{-6} \pm 10 \%$$

A third suspension with the χ_1 -axis vertical showed that $\chi_3 > \chi_2$ (numerically), but the anisotropy was too small for measurement on such a small crystal.

These results, however, are sufficient to confirm the known crystal structure, and together with it they will give the molecular anisotropy. The X-ray measurements prove that the molecule is completely plane, and have given the direction cosines which characterize its position in the crystal framework. The whole molecular structure is centrosymmetrical and pseudo-tetragonal, hence we may assume that $K_1 = K_2$ in the plane of the atomic nuclei. Now

$$\chi_1 = K_1 \alpha_1^2 + K_2 \alpha_2^2 + K_3 \alpha_3^2 = K_1(1 - \alpha_3^2) + K_3 \alpha_3^2,$$

$$\chi_2 = K_1 \beta_1^2 + K_2 \beta_2^2 + K_3 \beta_3^2 = K_1(1 - \beta_3^2) + K_3 \beta_3^2,$$

$$\chi_3 = K_1 \gamma_1^2 + K_2 \gamma_2^2 + K_3 \gamma_3^2 = K_1(1 - \gamma_3^2) + K_3 \gamma_3^2,$$

where α, β, γ are the direction cosines of K_1, K_2, K_3 referred to the principal directions of susceptibility χ_1, χ_2, χ_3 .

$$\chi_2 - \chi_1 = K_1(\alpha_3^2 - \beta_3^2) + K_3(\beta_3^2 - \alpha_3^2) = (K_3 - K_1)(\beta_3^2 - \alpha_3^2),$$

$$\chi_3 - \chi_1 = (K_3 - K_1)(\gamma_3^2 - \alpha_3^2),$$

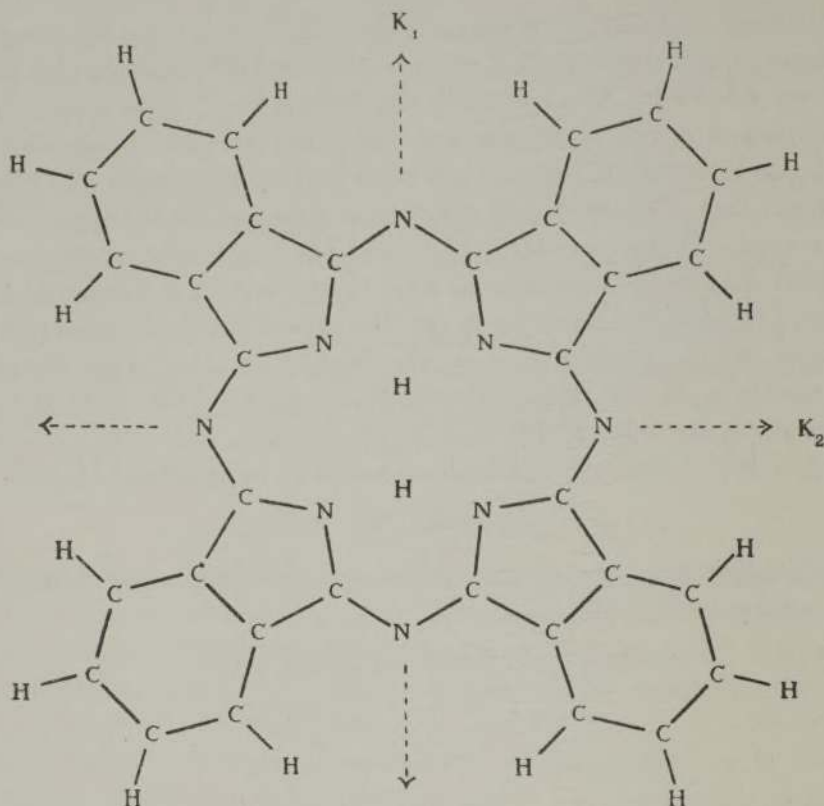


FIG. 1—Phthalocyanine molecule.

$\alpha_3, \beta_3, \gamma_3$ are the direction cosines of K_3 , which is normal to the plane of the molecule, and are given by

$$\alpha_3 = \sin 15\frac{1}{2} \cos \chi_N + \cos 15\frac{1}{2} \cos \omega_N = 0.035,$$

$$\beta_3 = \cos 15\frac{1}{2} \cos \chi_N - \sin 15\frac{1}{2} \cos \omega_N = -0.696,$$

$$\gamma_3 = \cos \phi_N = 0.717,$$

χ_N, ϕ_N, ω_N , the angles between the normal to the molecular plane and the a, b, c' axes respectively, were accurately obtained by Robertson (1936) from Fourier analysis.

Knowing $(\chi_2 - \chi_1)$ and $(\chi_3 - \chi_1)$, two estimates of $K_3 - K_1$ are obtainable.

$$(1) K_3 - K_1 = \frac{\chi_2 - \chi_1}{\beta_3^2 - \alpha_3^2} = -770 \times 10^{-6} \pm 5 \%,$$

$$(2) K_3 - K_1 = \frac{\chi_3 - \chi_1}{\gamma_3^2 - \alpha_3^2} = -773 \times 10^{-6} \pm 10 \%.$$

There are in the molecule (fig. 1) four complete individual benzene nuclei, each of which must contribute 60×10^{-6} towards the anisotropy of the phthalocyanine molecule. The central part of the molecule is a large closed ring of 8 carbon alternated with 8 nitrogen atoms, together with two hydrogen atoms, and this ring must be responsible for the rest of the anisotropy.

$$\begin{aligned} \Delta K_{\text{phthal.}} - 4\Delta K_{\text{benz.}} &= -(770 - 240) \times 10^{-6} \\ &= -530 \times 10^{-6}. \end{aligned}$$

Ordinary valency considerations account for all but 14 of the electrons in the central ring of atoms. These 14 electrons (analogous to the π electrons of aromatic compounds) must occupy orbits, in the plane of the molecule, of sufficient area to produce an anisotropy of 530×10^{-6} . As before, this area \bar{S} can be estimated by use of the formula

$$\Delta K = \frac{4 \cdot 248}{\pi} \cdot 14\bar{S},$$

which gives a mean orbital area of $28 \cdot 1 \text{ \AA}^2$ per electron. This may be compared with $7 \cdot 4 \text{ \AA}^2$, the area of the π -electron orbit in benzene, which is somewhat greater (fig. 2) than the actual area of the hexagon of carbon nuclei, $5 \cdot 0 \text{ \AA}^2$.

The area of the π -electron orbits in phthalocyanine, $28 \cdot 1 \text{ \AA}^2$, is also greater than the area of the central C—N ring, $23 \cdot 7 \text{ \AA}^2$, but it is of the same relative order, and it is definitely smaller than the area of the whole phthalocyanine molecule, or even than the whole molecule less the four benzene rings.

It seems probable that the electron density due to the π electrons is spread over an area roughly equivalent

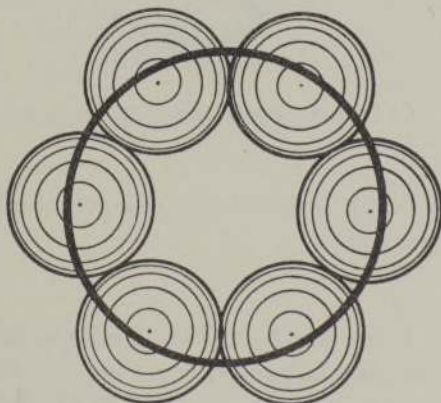


FIG. 2—Benzene nucleus showing plane and spherical orbits.

to (or somewhat larger than) that of the central closed carbon, nitrogen ring, and possibly to a smaller extent over the C—C bonds between the central ring and the attached benzene nuclei.

The interatomic distances obtained by Robertson (1936, p. 1204) from Fourier analysis indicate that the central ring is fully conjugated, while the C—C bonds between the central ring and the benzene rings are partially conjugated, having about 12–15 % double-bond character.

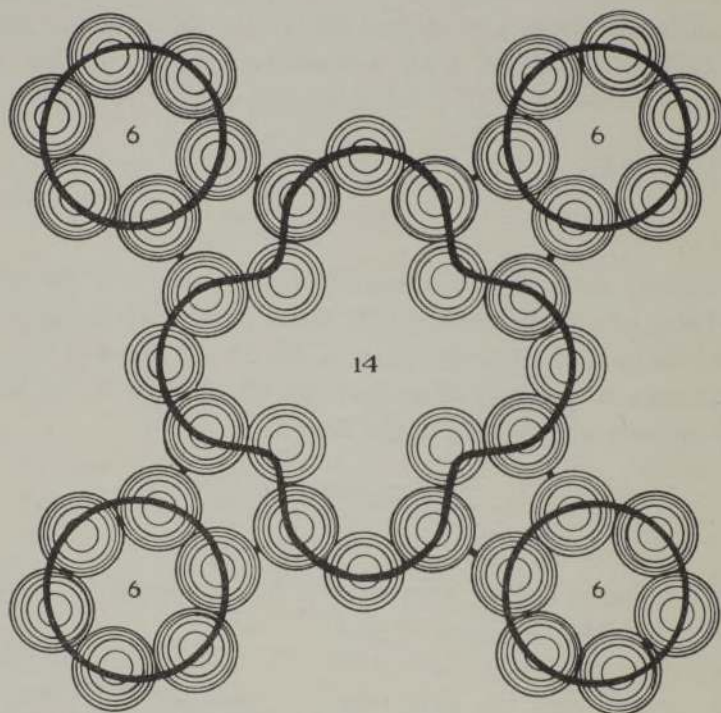


FIG. 3—Phthalocyanine framework showing spherical and plane orbits.

In fig. 3 are shown, diagrammatically, the π -electron orbits in phthalocyanine.

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SUMMARY

The remarkable anisotropy of benzene, cyanuric and phthalocyanine compounds may be explained on the assumption that, whereas the normal valency electrons behave as if they were spherically symmetrical and free to precess under the influence of any magnetic field, the π electrons occupy plane orbits which are free to precess only in their own plane. The radius of the s -electron orbits calculated from susceptibility data is about 0.7 Å, that of the plane orbits occupied by the benzene π electrons is 1.55 Å, which agrees well with the theory of molecular orbitals. The anisotropy of cyanuric compounds is only about one-half the value expected for complete conjugation, but in phthalocyanine the 14 π electrons in the central closed ring appear to occupy molecular orbitals of area a little larger than that of the central ring itself.

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