The Diamagnetic Sucseptibilities and Anisotropies of the Polynuclear Aromatic Compounds

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Introduction

Aromatic compounds show the large diamagnetic anisotropies, the values of the principal susceptibility normal to the planes of molecules are abnormally large compared to that in the planes. The phenomenon has been explained by the presence of the non-localized electrons in these molecules, one π-electron per aromatic carbon atom, which are free to circulate, under the influence of the magnetic field, from one atom to the other along the aromatic rings. The behaviour is closely analogous to the electric current induced in a conducting network.[1~8]

In general, the diamagnetic anisotropy for a molecule can be estimated from the magnetic data which are observed along the principal axes of a crystal, combined with the informations about the orientation of the molecules in it. Several investigations[9] for aromatic compounds have been made in this way. Such a method is the orthodox one, neverthless, it can not be applied to the substances whose crystal structures have not been fully analysed. Moreover, frequently, we can not obtain the single crystals large enough in size to be able to be used for the magnetic measurement, especially when the molecular weight becomes larger. In such a case, the specimens are made of fine crystals in the powder form, and it is merely the values of the mean susceptibility that we can know. Fortunately, however, in the case of the planar molecules as the condensed polynuclear aromatic compounds, it is able to evaluate approximately the diamagnetic anisotropies from the values of the mean susceptibility. The method has been devised by Hazato[10] and by Pacault[11].

Let K_1, K_2 and K_3 be the principal mole susceptibilities for a molecule, where K_1 and K_2 are those in the plane of molecule, and K_3 is that perpendicular to the plane. Then the mean mole susceptibility χ_M will be expressed by

$$\chi_M = 1/3\,(K_1+K_2+K_3) \qquad (1)$$

It can be assumed that $K_1 \fallingdotseq K_2$ for the planar structure of molecule. Then the diamagnetic anisotropy of the molecule is expressed as

$$\Delta K = K_3 - K_1 = 3\,(\chi_M - K_1) \qquad (2)$$

The anisotropic part of the susceptibility, ΔK, is due to the circulation of the π-electrons in the plane of molecule, whereas K_1 (and K_2) is the isotropic part and will be the sum of the atomic susceptibilities based on the distribution of electrons being spherical symmetry. The approximate expressions for K_1 have been made by several authors. Pauling[7] has assumed the atomic susceptibility of aromatic carbon, aside from the p_z-electron, being $3/4\,(-6.0\times10^{-6})$. On the other hand, Hazato and Pacault have used the Pascal's empirical formula in a modified way, i.e.,

$$\chi(\mathrm{C}=) = \chi(\mathrm{C}) + 1/4\cdot\lambda\,(\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}) = (-6.0+10.56/4)\times10^{-6} = -3.36\times10^{-6} \qquad (3)$$

was assumed by Hazato, and

$$\chi(\mathrm{C}=) = \chi(\mathrm{C}) + 1/2\cdot\lambda\,(\mathrm{C}=\mathrm{C}) = (-6.0+5.45/2)\times10^{-6} = -3.28\times10^{-6} \qquad (3)'$$

was assumed by Pacault. In this way, K_1 for hydrocarbons is expressed as

$$K_1 = \Sigma\chi(\mathrm{C}=) + \Sigma\chi(\mathrm{H}) \qquad (4)$$

Better results in the way of the latter authors are given than the former. In the present report, $\chi(\mathrm{C}=) = -3.36\times10^{-6}$ was used following Hazato, combined with $\chi(\mathrm{H}) = -2.93\times10^{-6}$.

1) E. Hückel, *Z. Physik.*, **83**, 632 (1933).
2) A. R. Ubbelohde, *Nature*, **132**, 1002 (1933).
3) F. London, *J. phys. radium.*, **8**, 397 (1937); *J. Chem. Phys.*, **5**, 837 (1937).
4) H. Brooks, *J. Chem. Phys.*, **9**, 463 (1941).
5) B. Pullman et al., *J. phys. radium.*, **12**, 652, 717 (1951); **13**, 15 (1952).
6) R. McWeeny, *Proc. Phys. Soc.*, **A64**, 261, 921 (1951).
7) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).
8) K. Lonsdale, *Proc. Roy. Soc.*, London, **A159**, 149 (1937).
9) K. S. Krishnan, *Nature*, **130**, 313, 698 (1932); K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London*, **A156**, 597 (1936); S. Banerjee, *Z. Krist.*, **100**, 316 (1939).
10) G. Hazato, *J. Chem. Soc. Japan*, **64**, 483 (1943); H. Shiba and G. Hazato, This Bulletin, **22**, 92 (1949).
11) A. Pacault, *Bull. Soc. Chim. France*, **1949**, D. 61.

Experimental

Materials.—A part of the materials was obtained from the commercial products, neverthless, most materials were synthesized by Mr. T. Handa in our laboratory. All of the materials were carefully purified by the usual method. In each case, the repeated sublimation *in vacuo* was applied to the last process of the purification. As the molecular weight increases, no good solvent can be found for the polynuclear aromatic compounds, in consequence, the ordinary method of purification including the dissolution process can not be applied. Even in such a case, the method of sublimation *in vacuo* gives the favourable results. Some details for the materials have been given in a previous report[12].

Magnetic Measurements.—The Gouy method was employed for the measurements of the magnetic susceptibility. The specimen tube was made of a cylindrical glass tube, which was separated into two sections by a glass partition. The upper half was packed with the sample, while the lower half was permanently evacuated. This was suspended between the poles of a magnet, hanging from an arm of an analytical balance, so that the lower end of the sample column was nearly at the centre of the poles, while the lower portion of the tube extended below the magnetic field. The dimension of the sample container was about 33 mm. in height (about half the length of the total tube) and about 0.094 sq. cm. in cross section, in one example. The diameter of the pole face is 20 mm., and the gap between the poles is 8 mm.

Taking water as the standard substance, the mass susceptibility, χ, is given by

$$\chi=(\kappa^*-\kappa_0)\frac{V}{F^*-F_0}\cdot\frac{F-F_0}{m}+\frac{\kappa_0}{d} \quad (5)$$

where m, d are the mass and the density, respectively, of the sample, κ^*, κ_0 are the volume susceptibilities of water and air respectively, F^*, F are the apparent changes in weight on application of the magnetic field when the tube is filled with water, and with the sample occupying the same volume V as water respectively, and F_0 is that for the empty tube. Hence, $V/(F^*-F_0)$ is the cell-constant. The values of κ^* and κ_0 were assumed to be -0.720×10^{-6} and $+0.0294\times10^{-6}$ respectively at 20°C. A constant magnetic field, about 23,000 oersteds was applied in every case. It is known by investigators that the accuracy of measurements on powdered samples is limited by the uniformity and reproducibility of packing. It seems preferable to pack the sample as close as possible.

Among a series of measurements, the calibration was checked with naphthalene from time to time. The mass susceptibility of naphthalene estimated in our experiment was $-(0.720\pm0.001)\times10^{-6}$.

Results

The results are shown in Table 1 for hydrocarbons as well as in Table 2 for quinones. In these tables, the values of the diamagnetic anisotropy calculated by equation (2) and (3) are given in column 6. The values for the low molecular weight members, taken from the International Critical Tables, are also shown for comparison.

For quinones, the calculations of ΔK were made by using the value of $+1.73\times10^{-6}$ for χ(O), with the assumption that the carbon atoms in the carbonyl radical would be aromatic; in consequence, χ(C) for these carbon atoms was also assumed to be -3.36×10^{-6}, instead of -6.00×10^{-6} for aliphatic carbon. This latter assumption is preferable, since the calculated value of ΔK for *p*-benzoquinone is not far from 40.6[13] which was evaluated by Lonsdale and Krishnan[9] from the anisotropy of the crystal, and ΔK calculated for anthraquinone is not far from 165 which was supposed by Banerjee[9]. Which assumption would be made, the difference will be small for compounds with the higher number of carbon atoms.

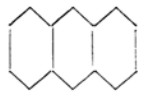
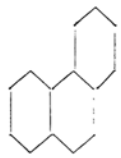
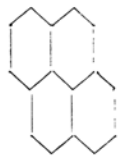
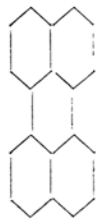
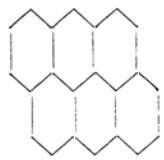
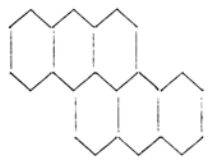
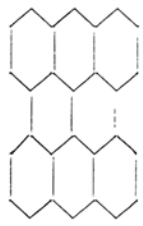
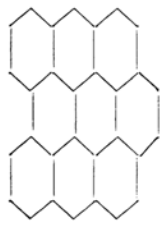
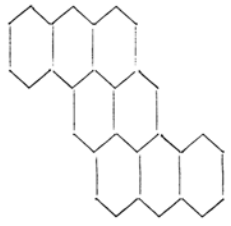
Table 1

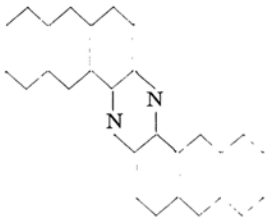
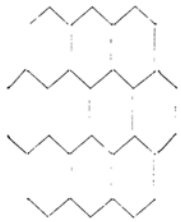
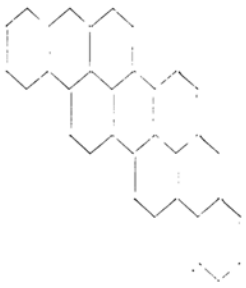
Diamagnetic Susceptibilities and Anisotropies of Condensed Polynuclear Aromatic Hydrocarbons

Substance			Mass Suscept. $(-\chi\cdot10^{-6})$	Mole Suscept. $(-\chi_M\cdot10^{-6})$	Aniso-tropy $(-\Delta K\cdot10^{-6})$	$\sqrt{\overline{r^2}}$ (Å)	(p)
Benzene	C_6H_6		0.712*	55.6	54	1.44	(6)
Naph-thalene	$C_{10}H_8$		0.717*	91.9	105	1.57	(10)

12) H. Inokuchi, S. Shiba, T. Handa, and H. Akamatu, This Bulletin, **25**, 229 (1952).

13) The factor -1×10^{-6} is to be understood with all values of susceptibility and anisotropy in the following discussion.

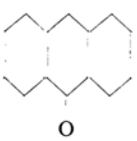
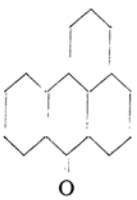
Anthracene	$C_{14}H_{10}$		0.726*	129.4	159	1.64 (14)
Phenanthrene	$C_{14}H_{10}$		0.718*	127.9	155	1.61 (14)
Pyrene	$C_{16}H_{10}$		0.731±0.001	147.9	197	1.70 (16)
Perylene	$C_{20}H_{12}$		0.662±0.002	166.8	193	1.51 (20)
Anthanthrene	$C_{22}H_{12}$		0.739±0.002	204.2	285	1.75 (22)
Dibenzpyrene	$C_{24}H_{14}$		0.706±0.002	213.6	276	1.65 (24)
Mesonaphthodianthrene	$C_{28}H_{14}$		0.612±0.001	214.6	238	1.42 (28)
Dibenzcoronene	$C_{30}H_{14}$		0.778±0.003	289.4	443	1.87 (30)
Pyranthrene	$C_{30}H_{16}$		0.709±0.002	266.9	358	1.68 (30)

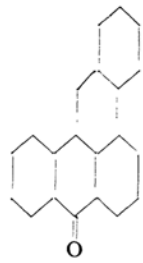
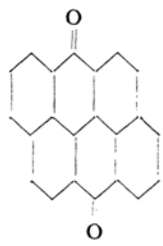
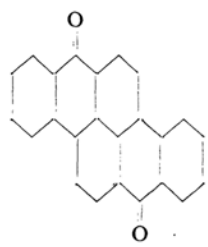
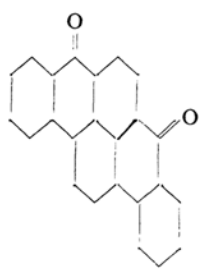
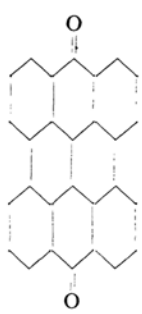
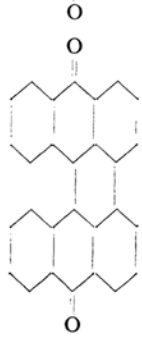
Indanthrazine	$C_{28}N_2H_{16}$		0.646±0.002	245.7	330	1.61	(30)
Ovalene	$C_{32}H_{14}$		0.888±0.007	353.8	616	2.12	(32)
Violanthrene	$C_{34}H_{18}$		0.641±0.002	273.5	320	1.49	(34)

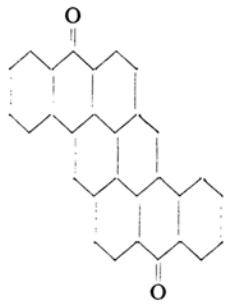
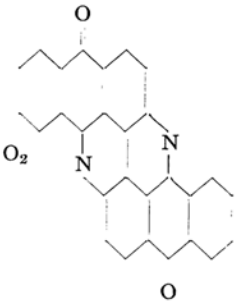
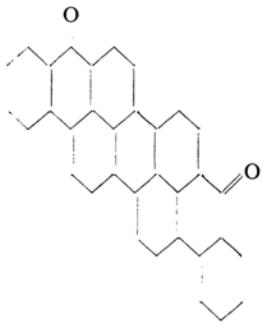
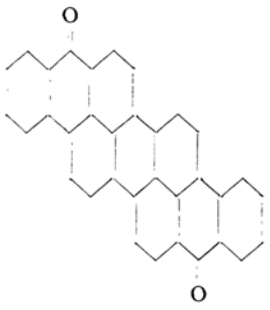
* International Critical Tables

Table 2

Diamagnetic Susceptibilities and Anisotropies of Condensed Polynuclear Quinones

Substance			Mass Suscept. $(-\chi\cdot10^{-6})$	Mole Suscept. $(-\chi_M\cdot10^{-6})$	Anisotropy $(-\Delta K\cdot10^{-6})$	$\sqrt{\bar{r}^2}$ (Å)	(p)
p-Benzoquinone	$C_6H_4O_2$		0.382*	41.3	39	1.24	(6)
Anthraquinone	$C_{14}H_8O_2$		0.575*	119.6	158	1.62	(14)
Phenanthrenequinone	$C_{14}H_8O_2$		0.502±0.001	104.5	113	1.38	(14)
Benzanthrone	$C_{17}H_{10}O$		0.620±0.003	142.9	175	1.56	(17)

Dibenz-phenan-throne	$C_{21}H_{12}O$		0.716±0.002	200.5	295	1.82 (21)
Anthan-throne	$C_{22}H_{10}O_2$		0.581±0.002	178.1	235	1.59 (22)
Dibenz-pyrene-quinone	$C_{24}H_{12}O_2$		0.551±0.001	183.1	212	1.44 (24)
iso-Dibenz-pyrene-quinone	$C_{24}H_{12}O_2$		0.586±0.001	194.6	247	1.56 (24)
Meso-naphtho-dianthrone	$C_{28}H_{12}O_2$		0.583±0.003	221.8	288	1.56 (28)
Helian-throne	$C_{28}H_{14}O_2$		0.497±0.003	189.9	175	1.21 (28)

Pyranthrone	$C_{30}H_{14}O_2$		0.616±0.003	250.3	335	1.62 (30)
Flavanthrone	$C_{28}N_2H_{12}O_2$		0.590±0.001	241.0	361	1.68 (30)
Violanthrone	$C_{34}H_{16}O_2$		0.449±0.003	204.8	159	1.05 (34)
iso-Violanthrone	$C_{34}H_{16}O_2$		0.473±0.002	215.9	193	1.16 (34)

* International Critical Tables

It will be seen from the results that, in general, the diamagnetic anisotropy becomes progressively large with the increase in the number of rings. However, the increment in the anisotropy by the increase in the number of rings is not made by a simple way, but strikingly depends upon the shape of the molecule or the way of the aromatic condensation. Therefore, to see the rate of increment in the anisotropy, it is desirable to know some quantity assigned to each one carbon atom or π-electron. Since the anisotropy is caused by the circulation of the π-electrons in the molecular plane, their contribution to the anisotropy can be expressed, conveniently, by the Langevin theory as,

$$\Delta K = -(Ne^2/4mc^2)\sum_p \overline{r^2} = -4.248\cdot10^{-10}\cdot p\cdot\overline{r^2} \quad (6)$$

where $\sqrt{\overline{r^2}}$ is the average effective radius of the π-electron orbitals, p is the number of the π-electrons, and the other symbols have the usual meanings. The calculated values of $\sqrt{\overline{r^2}}$ are given in the last column

in the tables with the values of p assumed.

For benzene, the average radius of the π-orbitals is calculated as 1.44 A., and this average may be compared with 1.39 A., the radius of the benzene nucleus itself. As the condensation of rings increases, from benzene, through naphthalene, anthracene, pyrene, anthanthrene, dibenzcoronene, to ovalene, the average π-orbital radii become progressively large. The final product of the aromatic condensation is to be found in graphite, whose average π-orbital radius is about 8 A., calculated from Krishnan's data[14] in the same way.

The large value of the average π-orbital radius means that some fractions of π-electrons occupy the orbits whose radii are larger than that of a single benzene ring, in other words, their mobile or non-localized character is increased in the statistical sense. This occurrs among the above molecules.

On the other hand, there are molecules whose average π-orbital radii are relatively small, notwithstanding the fact that they are made of a large number of rings. For violanthrene, as an example, $\sqrt{\overline{r^2}}$ is 1.49 A. which is merely comparable to benzene.

In Fig. 1, the average π-orbital radii are plotted against the number of π-electrons, refering to the molecular structures. It will be seen in this figure, that the molecules occupying the upper positions are made of the closely compact arrangement of rings, while the molecules occupying the lower positions are made of the extended or concave arrangement of rings. The molecules discussed above belong to the former group, while in the latter group the π-electrons must be more or less localized in the statistical sense.

Perylene and Meso-naphthodianthrene— It is worth while to comment on perylene and meso-naphthodianthrene. For perylene, the diamagnetic anisotropy has beeen evaluated by Shiba and Hazato[10], as ΔK (perylene) $/\Delta K$(naphthalene)$=1.96\sim2.02$, and from this result, they assumed that the perylene molecule has two predominant naphthalene nuclei and the central hexagon in this molecule has a special structure which does not contribute to the diamagnetic anisotropy. From the results of the calculation of the diamagnetic anisotropy by London's method, Hazato[15] showed that this argument is supported when it is assumed that the central hexagon bonds have nearly the single bond character. Moreover, when the central hexagon is assumed to be equivalent to the other rings, a little paramagnetism is anticipated[16]. In the usual chemical language, the perylene molecule is not made of an aromatically conjugated system of the molecule as a whole but separated into two naphthalene nuclei. (Fig. 2 a). When this is not the case, the molecule would have the quinoid structure with excess electrons. (Fig. 2 b). This leads to the localization of the π-electrons. Therefore it would not be unreasonable to anticipate that the diamagnetic anisotropy of perylene may be smaller than twice that of naphthalene.

The mole susceptibility of perylene has

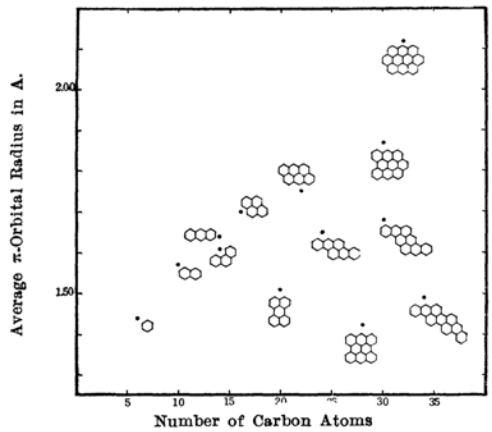


Fig. 1. The average π-orbital radii are plotted against the number of carbon atoms (or π-electrons), refering to the molecular structures.

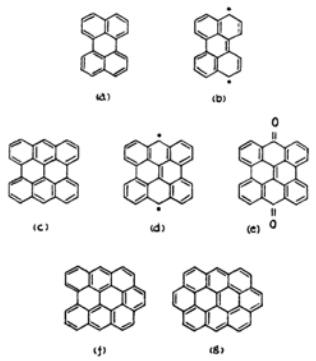


Fig. 2. (a) (b): Perylene, (c) (d): Meso-naphthodianthrene, (e): Meso-naphthodianthrone, (f): Dibenzcoronene, (g): Ovalene.

14) K. S. Krishnan, *Nature*, **133**, 174 (1934).

15) G. Hazato, This Bulletin, **22**, 151 (1949).

16) In the calculation by Hazato for this case, no definite value was obtained, neverthless, our recalculation shows that ΔK(perylene)/ΔK(naphthalene)$=-0.08$, neglecting the overlap integral.

been found to be 171 by Shiba and Hazato, while it is 165.0 by Pacault[17], and 166.8 in the present report. The smaller value of ΔK is evaluated from both of the latter rather than from the former; neverthless, the difference will not be large. Therefore, the contribution from the quinoid structure to the wave function of perylene will not be very large, at least from the magnetic standpoint.

Meso-naphthodianthrene is in the same situation as perylene. (Fig. 2 c, d). In this case, however, the diamagnetic anisotropy is much smaller than twice that of anthracene, i.e., $\Delta K(M.\ N.)/\Delta K(\text{anthracene})=1.5$. The average π-orbital radius is merely comparable to that of benzene. This means that the localization of π-electrons occurrs much more strongly in meso-naphthodianthrene than in perylene. This is in agreement with the empirical fact that the former is more chemically reactive than the latter, i.e., it is easy to synthesize ovalene from meso-naphthodianthrene by the reaction with maleic anhydride, while it is difficult to synthesize coronene from perylene.

In dibenzcoronene, the aromatically conjugated system can be completed at least of the molecule as a whole, (Fig. 2 f); then the diamagnetic anisotropy as well as the average π-orbital radius jumps to the higher value. This is further increased in ovalene. (Fig. 2 g).

The colour of meso-naphthodianthrene is deep green, while meso-naphthodianthrone is brownish green, dibenzcoronene is brown, and ovalene is reddish orange. It is interest that the former has the deepest colour among these. This may be associated to the structure in which the contribution from the large electric moment takes place; this leads to the quinoid type structure with the excess electrons in pairs making the formal charge. The triplet state may be conceivable too, whose paramagnetic contribution cancels the diamagnetic property in part. However, this fact has not yet been ascertained.

The similar discussion must also be extended to the molecules with long shaped structure, such as violanthrene, since their diamagnetic anisotropies are small.

Quinones

In the calculation of the average π-orbital radii of quinones, it was assumed that the π-electrons of all carbon atoms, including the carbonyl radical, contribute to ΔK. For *p*-benzoquinone, the average π-orbital radius is 1.24 A. when calculated with six π-electrons in this way, whereas 1.52 A. with four π-electrons omitting two combined to oxygen atoms. In the present report, the calculation followed the former way, and assumed that the difference in the values between *p*-benzoquinone and benzene is due to the localization of the π-electrons caused by the carbonyl radicals. In consequence, the evaluated values of the average π-orbital radii for quinones, in general, become a little smaller than that for the corresponding hydrocarbons. This difference ($\Delta\sqrt{\overline{r^2}}$) is about 0.2 A. This is the case of *p*-benzoquinone, phenanthrenequinone, anthanthrone, and dibenzpyrenequinone.

Neverthless, for meso-naphthodianthrone, the values of ΔK and $\sqrt{\overline{r^2}}$ are much larger than that of corresponding meso-naphthodianthrene. It will be understood from the discussion in the preceding section, when we remember that passing from meso-naphthodianthrene to meso-naphthodianthrone the aromatically conjugated system of the molecule as a whole can be completed, and this leads to the delocalization of excess electrons in the former. (Fig. 2 e).

The opposite case to this is seen, when passing from violanthrene to violanthrone. The diamagnetic anisotropy of violanthrone is abnormally small; the average π-orbital radius is only 1.05 A. In this case, again, the molecule can not be made of an aromatically conjugated system as a whole but separated into two benzanthrone nuclei. The overlapping effect of this and the elongated structure of this molecule strikingly decreases the diamagnetic anisotropy. The value of ΔK of violanthrone is not only far smaller than twice that of benzanthrone, but it is even smaller than that of benzanthrone itself.

From the results discussed above, it may be concluded that, when a molecule can not be made of an aromatically conjugated system as a whole but separated into two predominant nuclei, the larger the nuclei are, the more strongly the diamagnetic anisotropy falls off.

The Tables contain the results on a few aza-aromatic compounds[18]. The magnetic property of the aza-aromatic ring is quite like that of the benzene ring. This is clearly shown when comparing the result on flavanthrone with that on pyranthrone.

17) A. Pacault, *Ann. chim.* [12] **1**, 257 (1946).

18) In the calculation of K_1, $\chi(\text{N}=)=\chi(>\text{C}=\text{N}-)-\chi(\text{C}=)=[(-6.00-5.57+8.16)-(-3.36)]\times10^{-6}=-0.05\times10^{-6}$ was assumed, from the Pascal's constants and equation (3).

Summary

The magnetic susceptibilities of condensed polynuclear aromatic compounds with higher molecular weights (ten hydrocarbons and twelve quinones) have been measured by the Gouy method, and the diamagnetic anisotropies have been approximately evaluated.

The diamagnetic anisotropy becomes progressively large as the number of rings increases, when the aromatic condensation takes place in the manner of the closely compact arrangement of rings; while, when it is not the case, it depends strikingly upon the molecular structure.

When the diamagnetic anisotropy has a smaller value, notwithstanding the molecule is made of a large number of rings, the localization of the π-electrons or some other excited states must be assumed. Such a case is found, when a molecule is not made of the aromatically conjugated system as a whole but separated into two predominant nuclei, as meso-naphthodianthrene and violanthrone, or when a molecule is made of a long shaped structure as pyranthrene or violanthrene.

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