

The Diamagnetic Anisotropy of Aromatic Molecules

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We thus obtain for 17 percent additive binding $E_c = 32.8$; $E_0 = 37.85$ and $E = 36.62$ at 503.2° . For 20 percent additive binding $E_c = 24.9$; $E_0 = 30.29$; $E = 29.04$. Now defining three A 's by the following equations

$$k = A_c e^{-E_c/kT} = A_0 e^{-E_0/kT} = A e^{-E/kT}$$

we obtain Table VII.

These values are to be compared with the experimentally obtained specific reaction rate of Bonner, Gore and Yost.⁴ We change k from their units to cc mole⁻¹ sec.⁻¹ and so obtain $k = .52 = 1.64 \times 10^{15} e^{-33,900/k478.2}$; $2.8 = 1.49 \times 10^{15} e^{-33,900/k503.2}$ and $5.8 = 1.60 \times 10^{15} e^{-33,900/k513.2}$

By inspection of Table VII we see that A is independent of whether 20 percent or 17 percent additive binding is used. This is important since this means it is uniquely fixed by the potential function and depends on no arbitrary constant. If the percentage additive binding were raised to a fraction over 20 percent E would be lowered by a calorie to 28 kcal. and k would then agree rather well with the experimental values. The theoretical k would, however, not increase with temperature as fast as the experimental value does. Thus, if Bonner, Gore and Yost are, as they

TABLE VII.

% additive	T	k	$A_c \times 10^{10}$	$A_0 \times 10^{13}$	$A \times 10^{12}$
17	478.2	7.44×10^{-5}	7.36	1.50	4.11
17	503.2	5.12×10^{-4}	9.06	1.46	4.16
17	513.2	1.03×10^{-3}	9.64	1.37	4.09
20	478.2	2.28×10^{-1}	5.51	1.60	4.30
20	503.2	1.01	6.61	1.46	4.17
20	513.2	1.79	7.26	1.43	4.21

believe, actually measuring the reaction rate here calculated and if their values of k are dependable then our calculated A is too small by a factor of ≈ 350 . A would be increased by this amount if the three lowest frequencies are actually around 50 wave numbers instead of the calculated values. Such a change would also reduce the excess ($E_0 - E_c$) of the zero-point energy in the activated state over that in the initial state to practically zero. More experiments seem necessary before any of these quantities can be assigned from experiment with assurance. The corresponding isotopic reactions will also be useful in calculating $E_0 - E_c$. Extensive accurate data on reactions of this type will be particularly valuable in determining the accuracy and in suggesting methods for improving the calculation of potential functions of activated complexes.

The Diamagnetic Anisotropy of Aromatic Molecules

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Values of the diamagnetic anisotropy of benzene and other aromatic hydrocarbon molecules are calculated on the basis of the assumption that the p_z electrons (one per aromatic carbon atom) are free to move from carbon atom to adjacent carbon atom under the influence of the impressed fields. When combined with the assumed values for the contributions of the other electrons (-2.0×10^{-6} for hydrogen, -4.5×10^{-6} for aromatic carbon, -6.0×10^{-6} for aliphatic carbon) these lead to principal diamagnetic susceptibilities of molecules in approximate agreement with the available experimental data. The diamagnetic anisotropy of graphite is also discussed.

CERTAIN diamagnetic crystals, such as bismuth and graphite, show pronounced diamagnetic anisotropy, the susceptibility being of normal magnitude in the basal plane and abnormally large in the direction perpendicular to this plane. A similar phenomenon is shown by

crystals of aromatic substances. It has been pointed out by Krishnan and his collaborators¹ that the magnitudes and orientations of the principal axes of the susceptibility ellipsoid of

* Contribution No. 555.

¹ (a) K. S. Krishnan, Proc. Ind. Sci. Cong., Madras Session, January, 1929; (b) K. S. Krishnan, B. C. Guha and S. Banerjee, Phil. Trans. Roy. Soc. **A231**, 235 (1933); (c) K. S. Krishnan and S. Banerjee, *ibid.* **A234**, 265 (1935).

such a crystal are determined by the values of the principal susceptibilities of the molecules of the aromatic substance and by the orientations of the molecules relative to the crystal axes. The susceptibility ellipsoids of the aromatic molecules are found to be approximately prolate ellipsoids of revolution, with the long axis normal to the plane of the ring system. As a result of the valuable investigations of Krishnan and his collaborators this phenomenon has been made the basis of an important auxiliary method for determining the structure of crystals.^{1, 2}

A qualitative explanation of these abnormally large diamagnetic susceptibilities as arising from the Larmor precession of electrons in orbits including many nuclei³ has come to be generally accepted. With the aid of simple assumptions, I have now developed this idea into an approximate quantitative treatment, described below.

Benzene

The Hamiltonian function for an electron in a constant magnetic field of strength H parallel to the z axis is⁴

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}' + \mathcal{H}'', \quad (1)$$

in which \mathcal{H}^0 is the Hamiltonian function for zero field strength,

$$\mathcal{H}' = -(He/2mc)(xp_y - yp_x), \quad (2)$$

and
$$\mathcal{H}'' = (H^2e^2/8mc^2)(x^2 + y^2). \quad (3)$$

The contribution of the electron to the diamagnetic susceptibility of the system can be calculated by the methods of quantum-mechanical perturbation theory, a second-order perturbation treatment being needed for the term in \mathcal{H}' and a first-order treatment for that in \mathcal{H}'' . In case that the potential function in \mathcal{H}^0 is cylindrically symmetrical about the z axis, the effect of \mathcal{H}' vanishes, and the contribution of the electron to the susceptibility (per mole) is given

by the Pauli expression, resulting from \mathcal{H}'' ,

$$\chi = -(Ne^2/4mc^2)(\rho^2)_{av}, \quad (4)$$

in which $(\rho^2)_{av}$ is the mean square of the distance of the electron from the z axis. This expression is valid for atoms and monatomic ions, the z axis being passed through the nucleus. It is not applicable (without correction for the term in \mathcal{H}') to molecules. For most molecules a satisfactory approximate treatment can be used which consists in assigning electrons to the nearest nucleus, Eq. (4) being applied to the electrons about each nucleus.

Of the forty-two electrons of the benzene molecule, twelve (the carbon K electrons) make no appreciable contribution to the magnetic susceptibility. Twenty-four of the L electrons (which may be considered to be involved in electron-pair bonds between adjacent atoms) are in orbitals which are symmetric with respect to reflection in the plane of the nuclei. It is probable that the contribution of these to the magnetic susceptibility is normal. The remaining six L electrons, which give to benzene its characteristic electronic structure and properties,⁵ occupy orbital wave functions which are antisymmetric with respect to reflection in the plane of the nuclei. The probability distribution function for these electrons is large only in two ring-shaped regions, one above and one below the carbon hexagon. We may well expect that in these regions the potential function representing the interaction of an electron with the nuclei and other electrons in the molecule would be approximately cylindrically symmetrical with respect to the hexagonal axis of the molecule, the electron, some distance above or below the plane of the nuclei, passing almost imperceptibly from the field of one carbon atom to that of the next. Under these conditions the contribution of each of these six electrons to the susceptibility with the magnetic field normal to the plane of the nuclei would be given by Eq. (4), with ρ measured from the hexagonal axis of the molecule, and it would hence be very large. On the other hand, because of the nodal plane of the wave functions these electrons would make only a very small contribution to the susceptibility

² S. Bhagavantam, Proc. Roy. Soc. **A124**, 545 (1929); S. Banerjee, Ind. J. Phys. **4**, 557 (1930); K. S. Krishnan, Nature **130**, 313, 698 (1932); K. S. Krishnan and S. Banerjee, ibid. **131**, 653 (1933); **132**, 968 (1933); Zeits. f. Krist. **91**, 173 (1935); K. Lonsdale, Nature **137**, 826 (1936); N. Ganguli, Zeits. f. Krist. **93**, 42 (1936).

³ P. Ehrenfest, Physica **5**, 388 (1925); Zeits. f. Physik **58**, 719 (1929); C. V. Raman, Nature **123**, 945 (1929); **124**, 412 (1929); C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. **A113**, 511 (1927).

⁴ See, for example, J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, 1932).

⁵ E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

with the field in the nuclear plane. There would thus arise a large diamagnetic anisotropy of the molecule. If we use for $(\rho^2)_{av}$ the value R^2 , in which R is the distance from the axis to the carbon nuclei, 1.39Å, the anisotropy is calculated to have the value $\Delta K = -49.2 \times 10^{-6}$, which is in reasonably good agreement with the experimental value for benzene,^{1b} $\Delta K = -54 \times 10^{-6}$.

A more detailed consideration may be given this argument by evaluating the terms corresponding to \mathcal{H}' and \mathcal{H}'' with the use of assumed expressions for the wave functions. Using hydrogen-like $2p_z$ wave functions, the term corresponding to \mathcal{H}'' (Eq. (4)) has the value -49.2×10^{-6} for large values of the effective nuclear charge, the absolute value increasing with decrease in the effective nuclear charge, as a result of the greater contribution of large radii to $(\rho^2)_{av}$. The term in \mathcal{H}' can be represented by means of the approximate second-order perturbation theory⁶ as

$$\chi' = [(xp_y - yp_x)^2]_{00} / ((W_m)_{av} - W_0), \quad (5)$$

in which the numerator represents the diagonal matrix element for the normal state under consideration, W_0 the energy of this state, and $(W_m)_{av}$ an average energy for significant excited states. It is found on evaluating this expression that it is small for reasonable values of the effective nuclear charge. However, this expression as well as that of Eq. (1) are rather sensitive to changes in the assumed wave functions, and there is little prospect at present of carrying out an accurate theoretical calculation of the susceptibility.

Condensed aromatic ring systems

We may now calculate the magnetic anisotropy of other aromatic hydrocarbons in the same way as for benzene, making 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. Our problem is equivalent to that of calculating the magnetic effect of the currents induced in a conducting network. In benzene we have assumed the induced current to flow from atom to atom along circular arcs. In large condensed ring systems, such as graphite, the current would be assumed to flow along

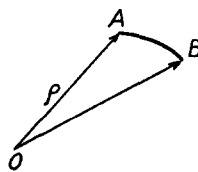


FIG. 1.

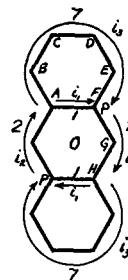


FIG. 2. Induced currents in anthracene.

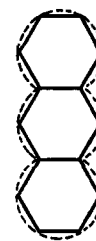


FIG. 3. Assumed path of induced currents in anthracene.

straight lines between adjacent atoms. In order to simplify the calculation we shall first consider rectilinear hexagonal nets, and then make a small correction by replacing the outermost lines by circular arcs. We assume in all cases that the electrons are uniformly distributed along the segments of the network, the linear density of electrons being σ .

Let us consider anthracene as an example. One solution of Maxwell's equations corresponding to a magnetic field parallel to the z axis, with strength increasing linearly with the time, involves an electric field acting in a direction in the xy plane at right angles to the radius vector ρ measured from the z axis and with strength proportional to ρ . The integrated ponderomotive force for a segment AB of a conductor is accordingly proportional to the area swept out by the radius vector ρ , in this case OAB . Using as our unit the area of one-sixth of a carbon hexagon, the integrated ponderomotive forces for anthracene (Fig. 2) are $P_1=1$ (for the segment AF), $P_2=2$ (for FGH), and $P_3=7$ (for $ABCDEF$), with values for the other segments given by the center of symmetry of the molecule and field. In addition we must introduce an auxiliary potential at the junction F (relative to A) represented by the symbol p . The effective resistances of the circuits, arising from the inertia of the electrons, are proportional to the lengths of the segments, and have the values $R_1=1$, $R_2=2$, and $R_3=5$. We thus obtain the equations

$$\begin{aligned} i_1 &= 1 - p, \\ 2i_2 &= 2 + p, \\ 5i_3 &= 7 - p \end{aligned}$$

for the currents i_1 , i_2 , and i_3 , together with the conservation equation

⁶ L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics*, Sec. 27e.

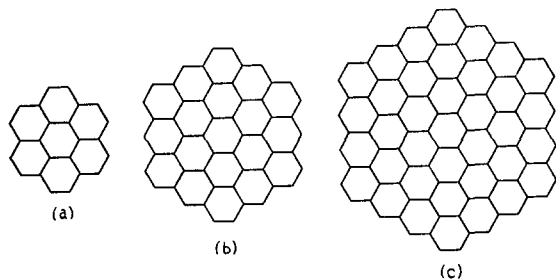


FIG. 4. The aromatic hydrocarbons (a) $C_{24}H_{12}$, (b) $C_{64}H_{18}$, and (c) $C_{96}H_{24}$.

$$i_2 = i_1 + i_3.$$

The values found on solution of these equations are $i_1 = 3/17$, $i_2 = 24/17$, and $i_3 = 21/17$. These correspond to a completed circuit i_1 about one hexagon and another completed circuit i_3 about three hexagons, the strength of the equivalent magnetic dipole being $66/17$. A similar calculation for a benzene hexagon gives the value 1; the quantity $k = 66/17$ accordingly represents the relative strengths of the induced magnetic dipoles for the anthracene network of three hexagons and the benzene circuit of one hexagon, difference in the linear electron density σ being neglected.

To obtain the susceptibility difference ΔK we make the following calculation. For naphthalene and higher aromatic hydrocarbons the average C—C distance⁷ is 1.41 Å, corresponding to $\Delta K = -38.0 \times 10^{-6}$ for a six-electron hexagon. In general we write for ΔK the expression

$$\Delta K = -38.0 \times 10^{-6} \times k \sigma f, \quad (6)$$

in which σ is the electron density per C—C bond and f a correction factor described below. Values of σ as well as of k are included in Table I; for

⁷ L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

anthracene, for example, σ has the value $14/16$, there being 14 p_z electrons and 16 C—C segments in the network. The factor f is designed to correct for the assumption that the electrons move along rectilinear paths between the carbon atoms. In benzene we assumed the transit from atom to atom to be along circular arcs. For the condensed ring systems we may correspondingly replace the outermost rectilinear segments by circular arcs, as shown in Fig. 3 for anthracene. This introduces a correction⁸ of 23 percent ($f = 1.23$), leading to $\Delta K = -159 \times 10^{-6}$ for anthracene. Table I includes the results of a similar treatment of several hydrocarbons.

In order to predict approximate values of the principal susceptibilities K_1 ($=K_2$) and K_3 ($=K_1 + \Delta K$) of these substances we may adopt the following empirical procedure. The molal susceptibility of H_2 is -4.00×10^{-6} ; we accept -2.00×10^{-6} for H bonded to C. The atomic susceptibility of diamond is -6.00×10^{-6} ; we accept this for aliphatic carbon. Now in the aliphatic carbon atom there are four L electrons contributing to the susceptibility in all directions, whereas in the aromatic carbon atom only three remain to be considered, the fourth being involved in the calculation of ΔK . For aromatic carbon, aside from the p_z electron, we accordingly assume the atomic susceptibility -4.5×10^{-6} . The principal susceptibilities of a hydrocarbon are thus given by the approximate expressions

$$K_1 = K_2 = -(2.0 n_H + 6.0 n_{C_{al}} + 4.5 n_{C_{ar}}) \times 10^{-6} \quad (7)$$

and

$$K_3 = K_1 + \Delta K, \quad (8)$$

⁸ The error introduced by using the values of relative currents for rectilinear segments is small.

TABLE I.

	σ	k	$-\Delta K \times 10^6$	$-K_1 \times 10^6$	$-K_3 \times 10^6$
Benzene, C_6H_6	1	1	49	39	88
Naphthalene, $C_{10}H_8$	10/11	12/5	104	61	165
Anthracene, phenanthrene, $C_{14}H_{10}$	7/8	66/17	159	83	242
Pyrene, $C_{16}H_{10}$	16/19	84/13	237	92	329
Naphthacene, chrysene, etc., $C_{18}H_{12}$	6/7	156/29	214	105	319
Triphenylene, $C_{18}H_{12}$	6/7	60/11	217	105	322
Perylene, $C_{20}H_{12}$	5/6	111/13	314	114	428
Picene, dinaphthanthracene, etc., $C_{22}H_{14}$	11/13	227/33	268	127	395
$C_{24}H_{12}$	4/5	52/3	572	132	704
$C_{64}H_{18}$	3/4	2667/29	2770	279	3050
$C_{96}H_{24}$	8/11	67333/227	8200	480	8680

TABLE II.

	$-K_1 \cdot 10^6$	Observed $-K_2 \cdot 10^6$	$-K_3 \cdot 10^6$	Calculated $-K_1(K_2) \times 10^6$	$-K_3 \cdot 10^6$
Benzene, C_6H_6	37	37	91	39	88
Durene, $C_{10}H_{14}$	77	86	141	79	128
Hexamethylbenzene, $C_{12}H_{18}$	101	103	164	99	148
Hexaethylbenzene, $C_{18}H_{30}$	165	165	231	159	208
Biphenyl, $C_{12}H_{10}$	67	67	175	74	172
Terphenyl, $C_{18}H_{14}$	98	98	260	109	256
Quaterphenyl, $C_{24}H_{18}$	129	129	345	144	340
1,3,5-Triphenylbenzene, $C_{24}H_{18}$	131	131	347	144	340
Fluorene, $C_{13}H_{10}$	73	73	194	80	178
Naphthalene, $C_{10}H_8$	39	43	187	61	165
Anthracene, $C_{14}H_{10}$	46	53	273	83	242
Phenanthrene, $C_{14}H_{10}$	74	74	240	83	242
Pyrene, $C_{16}H_{10}$	81	81	303	92	329
Chrysene, $C_{18}H_{12}$	88	88	306	105	319
1,2; 5,6-Dibenzanthracene, $C_{22}H_{14}$	110	110	358	127	395

in which n_H , n_{Cal} , and n_{Car} represent the numbers of atoms of these kinds in the molecule.⁹ Values calculated in this way are included in Tables I and II.

The hydrocarbons $C_{24}H_{12}$, $C_{54}H_{18}$, and $C_{96}H_{24}$ included in the table have the hexagonal symmetry D_{6h} , as shown in Fig. 4. It is interesting to note that the shape of the molecule has a large effect on the susceptibility; ΔK for the nearly circular molecule $C_{24}H_{12}$ is over twice that for the long molecules picene, etc. ($C_{22}H_{14}$), although the molecules differ only a little in composition. Pyrene (compared with naphthalene) shows the same effect. Aside from this, the configuration of the molecule is of little significance, the susceptibilities for isomers such as anthracene and phenanthrene being the same. Branching of the chain of benzene residues has a small effect (compare naphthalene and triphenylene).

Comparison with experiment

In Table II there are given the available experimental values of the principal susceptibilities of aromatic hydrocarbon molecules, from the papers of Krishnan and his collaborators.^{1b, 1c, 10} It should be mentioned that in some cases the values have been obtained from crystal susceptibilities in a straightforward manner, with

⁹ The expressions could probably be made more accurate by the introduction of various constitutive correction terms (such as corresponding to Pascal's system). At present it does not seem worth while to attempt to refine the simple and straightforward treatment given above.

¹⁰ The values for hexaethylbenzene are those given by N. Ganguli, *Zeits. f. Krist.* **93**, 42 (1936), and for 1,2; 5,6-dibenzanthracene those given by K. S. Krishnan and S. Banerjee, *Zeits. f. Krist.* **91**, 173 (1935).

the use of the results of x-ray investigations of molecular orientations, but that in other cases the values given depend on various assumptions (such as that $K_3 - K_1$ for phenyl and phenylene groups has the value found for benzene). It is seen that with certain exceptions mentioned below the observed and calculated values agree to within about 10 percent, the disagreement probably being due in part to experimental error and in part to theoretical inaccuracy.

The largest differences between calculated and observed values are shown by naphthalene and anthracene. I feel confident that the differences are due to errors in the reported experimental values, especially since good agreement between experiment and theory is found for phenanthrene.

The principal susceptibilities of graphite, per mole of carbon atoms, are reported¹¹ as $K_1 = -5 \times 10^{-6}$ and $K_3 = -275 \times 10^{-6}$. It is to be noted that the value of K_1 is less than for diamond (-6×10^{-6}), and agrees with our assumed value -4.5×10^{-6} to within the accuracy of its determination. The very large magnetic anisotropy of graphite shows that the p_z electrons are free to move over large areas of the hexagonal network of carbon atoms in the crystal. Extrapolating from the values of Table I, we find that molecules about 40 Å in diameter would have an anisotropy equal to that observed for graphite. It is interesting that the anisotropy and the average susceptibility of graphite are decreased by decreasing the size of the crystal grains.¹²

¹¹ K. S. Krishnan, *Nature* **133**, 174 (1934).

¹² S. Paramasivan, *Ind. J. Phys.* **4**, 139 (1929); K. S. Krishnan and N. Ganguli, *Current Science* **3**, 472 (1935).