

and let B denote the scalar divergence of the vector B^p , so

$$B = \frac{1}{\sqrt{(-g)}} \sum_p \frac{\partial \mathfrak{B}^p}{\partial x^p}.$$

Then the following four identical relations exist :

$$-A_p + B\phi_p + \sum_q B^q M_{pq} + C_p = 0 \quad (p = 0, 1, 2, 3) \quad (35)$$

where it is obvious that the equations $C_p = 0$ are consequences of the equations $A_{pq} = 0$ and $B^p = 0$, or the four equations of motion of a particle carrying electric and magnetic charge are consequences of the ten gravitational equations and the four electromagnetic equations.

Magnetic Double-Refraction in Liquids. Part I.—Benzene and its Derivatives.

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1. *Introduction.*

Many organic liquids exhibit a feeble double-refraction when they are placed in a strong magnetic field and a beam of light traverses the substances in a direction transverse to the lines of force. The magnitude of this effect, which was discovered in 1907 by Cotton and Mouton, depends very largely on the chemical structure of the molecule. Hydrocarbons belonging to the aliphatic series and the aromatic series are strikingly different in their behaviour; hexane, for instance, showing no detectable effect, while benzene is an example of a liquid showing a measurable double-refraction. We propose in the series of papers of which this is the first, to discuss this phenomenon in its relation to the structure of molecules and their magnetic properties. For this purpose we shall use the theory of Langevin, which explains magnetic double-refraction as an effect arising from the orientative action of the field on the molecules (assumed to be magnetically and optically anisotropic) and connects the absolute value of the Cotton-Mouton constant with the values of the optical refractivity and of the magnetic susceptibility of the molecule along three mutually perpendicular axes. To enable the formula of Langevin to be used

for the purpose of calculating the absolute value of the Cotton-Mouton constant, it is necessary to have data concerning, firstly, the magnetic character of the molecule, and, secondly, its optical anisotropy. In regard to the latter, we propose to utilise the data obtained from observations on light-scattering in the liquids concerned. In regard to the magnetic anisotropy of the molecules, we shall endeavour to connect the indications furnished by the data on magnetic double-refraction with considerations of atomic and molecular structure and the well-known theory of diamagnetism, also due to Langevin.

2. Theory of Magnetic Double-Refraction.

We shall here merely quote the formula due to Langevin, the derivation of which is very conveniently set out in a recent article by Debye.* The Cotton-Mouton constant C_m of double-refraction is given by the relation

$$C_m = \frac{n_p - n_s}{\lambda H^2} \\ = \frac{3(n_0^2 - 1)^2}{80\pi n_0 \lambda k T \nu} \cdot \frac{[(A - B)(A' - B') + (B - C)(B' - C') + (C - A)(C' - A')]}{(A + B + C)^2}, \quad (1)$$

where A, B, C are the moments induced along the three mutually perpendicular axes of the optical ellipsoid of the molecule by unit electric force in the incident light-waves, acting respectively along the three axes, and A', B', C' are the magnetic moments induced in the molecule by unit magnetic force acting in the same three directions. H is the acting magnetic field, λ is the wave-length of the light, k is the Boltzmann constant, T the absolute temperature, ν the number of molecules per unit volume, n_0 the refractive index of the liquid outside the field, and n_p and n_s are the principal refractive indices in the field. The quantities A, B, C are connected with the refractive index n_0 of the liquid by the relation

$$\frac{A + B + C}{3} = \frac{3}{4\pi\nu} \cdot \frac{n_0^3 - 1}{n_0^2 + 2}. \quad (2)$$

The quantities A', B', C' are connected with the magnetic susceptibility of the medium by the relation

$$\frac{A' + B' + C'}{3} = \frac{\chi}{\nu}, \quad (3)$$

where χ is the susceptibility per unit volume.

It will be noticed that the Cotton-Mouton constant depends essentially on the differences of the magnetic susceptibilities of the molecules along the three directions which form the axes of the optical ellipsoid of the molecule.

* P. Debye, 'Marx's Handbuch der Radiologie,' vol. 6, pp. 754-76.

3. The Optical Anisotropy of the Molecule.

Observations on the state of polarisation of the light scattered by a gas or vapour enables us to evaluate directly an expression which depends on the differences (A - B), (B - C), and (C - A) between the optical properties of the molecule along its principal optical axes. The light scattered by an ideal spherically symmetrical molecule in a direction transverse to the incident unpolarised beam would be completely polarised. In all actual cases, however, the light so scattered is imperfectly polarised, indicating that the molecule is not optically isotropic. The state of polarisation is usually indicated by the ratio of the intensities of the two components of vibration in the scattered light. The ratio r of the intensity of the feeble component to the stronger component is connected with the values of A, B, C, by the relation

$$r = \frac{6[(A - B)^2 + (B - C)^2 + (C - A)^2]}{10(A + B + C)^2 + 7[(A - B)^2 + (B - C)^2 + (C - A)^2]}. \quad (4)$$

In the case of dense fluids, the problem of determining the relation between the optical anisotropy of the molecule and the state of polarisation of the transversely scattered light is not quite simple, as we have to take into account the influence of neighbouring molecules on each other and the effect of local fluctuations of density and molecular orientation on the optical field at any point in the medium. Various theories differing mainly in detail have been proposed, and the question how far they are in agreement with the available observations on light-scattering has been discussed in a recent paper by one of us.* Two formulæ of nearly identical form have been proposed, connecting the effective anisotropy of the molecule in the liquid state with the state of polarisation of the scattered light. The first formula is

$$r = \frac{6[(A - B)^2 + (B - C)^2 + (C - A)^2]}{10kT\beta\nu\left(\frac{n_0^2 + 2}{3}\right)^2 (A + B + C)^2 + 7[(A - B)^2 + (B - C)^2 + (C - A)^2]}, \quad (5)$$

where β is the compressibility of the medium.

A second formula which has been proposed is

$$r = \frac{6[(A - B)^2 + (B - C)^2 + (C - A)^2]}{10kT\beta\nu (A + B + C)^2 + 7[(A - B)^2 + (B - C)^2 + (C - A)^2]}. \quad (6)$$

The quantity δ given by the expression

$$\delta = \frac{[(A - B)^2 + (B - C)^2 + (C - A)^2]}{(A + B + C)^2} \quad (7)$$

* K. S. Krishnan, 'Proc. Ind. Assn. Cultn. Sc.', vol. 9, p. 251 (1926).

defines the optical anisotropy of the molecule and should be the same for the vapour and the liquid state. For many substances, however, the value of δ calculated by either formula from the scattering by the liquid is rather less than that calculated from the vapour, indicating that the effective optical anisotropy of the molecules may be diminished by reason of their close packing or actual association in the liquid. For this reason it seems appropriate, in any discussion bearing on the liquid state, to consider the values of the molecular anisotropy determined from observations on light-scattering in liquids. An extensive and careful study of the scattering in no fewer than 65 different liquids has been recently carried out in the authors' laboratory.* We propose to utilise the data thus gathered in our discussion of magnetic double-refraction.

The data available are not sufficient to decide absolutely whether formula (5) or formula (6) is to be preferred. Instead of rejecting one or the other, it seems preferable to retain and use both formulæ and to compare the results thus obtained.

4. *The Cases of Hexane and Benzene.*

Observations on light-scattering both in vapours and in liquids indicate that the hydrocarbons of the paraffin series exhibit a smaller degree of optical anisotropy than those of the aromatic series. The depolarisation factor r for the vapours of hexane and cyclohexane are 1.68 per cent. and 0.86 per cent. respectively. The corresponding values of r for liquid hexane and liquid cyclohexane are 9.9 per cent. and 8 per cent. The values of r for benzene vapour and liquid are respectively 4.4 per cent. and 47 per cent., being thus considerably larger than for either hexane or cyclohexane. From the value of r the value of δ may be easily calculated for the substances mentioned.

Table I.

	Benzene.	Hexane.	Cyclohexane.
$\delta \times 10^3$ from vapour	77	28.6	14.5
$\delta \times 10^3$ from liquid	{ 1st formula, equation (5)	8.9 ₅	6.5
	{ 2nd formula, equation (6)	5.3	3.6
Refractive index	1.505	1.378	1.429
C_m	5.90×10^{-13}	Not detectable	Not detectable

* K. S. Krishnan, 'Phil. Mag.', vol. 50, p. 697 (1925).

It will be noticed that in the case of hexane and cyclohexane, δ for the liquid is strikingly less than δ for the vapour. The difference is not so conspicuous in the case of benzene vapour and liquid, and, indeed, is of the opposite sign when formula (5) is used to calculate δ .

In the numerator of the expression for δ the expression

$$[(A - B)^2 + (B - C)^2 + (C - A)^2]$$

appears, while in that for the Cotton-Mouton constant the expression

$$[(A - B)(A' - B') + (B - C)(B' - C') + (C - A)(C' - A')]$$

occurs. It will be seen that the differences in the value of the Cotton-Mouton constant for the three substances are of a larger order of magnitude than those in the value of δ . The molecular refractivities and magnetic susceptibilities of the three substances are not very different. Hence, in order to explain the great differences in the value of the Cotton-Mouton constant, it is necessary to assume that the differences in the magnetic anisotropy of benzene and hexane are not less pronounced than the differences in their optical anisotropy. In fact, the data compel us to assume that hexane is practically isotropic magnetically, and that benzene, on the other hand, exhibits a remarkable degree of magnetic anisotropy.

An interesting sidelight on the relation between chemical structure and magnetic anisotropy of carbon compounds is furnished by the observations of Owen* and Honda and Také Soné† on the diamagnetic properties of the element carbon in the two forms of diamond and graphite. These authors have found that diamond, as might be expected from the fact that it belongs to the cubic system, shows no diamagnetic anisotropy. Graphite, on the other hand, shows a very large magnetic anisotropy, its susceptibility parallel to the hexagonal axis being about seven times as large as in perpendicular directions.

5. Calculation of the Cotton-Mouton Constant.

In order to evaluate absolutely the value of the Cotton-Mouton constant, we shall now assume that the benzene molecule has an axis of optical symmetry. This seems justifiable, particularly in view of the fact that chemical evidence shows that the six carbon atoms and the six hydrogen atoms in the ring are all equivalent. If the ring were a plane structure, then the axis of symmetry would obviously be the six-fold axis perpendicular to the plane of the ring. On

* M. Owen, 'Ann. der Physik,' vol. 37, p. 657 (1912).

† Kōtarō Honda and Také Soné, 'Sc. Rep. Tōhoku Imperial Univ.,' series I, vol 2, p. 25 (1913).

the other hand, even if the configuration of the molecule were a puckered ring in which alternate carbon atoms lie above and below a certain plane, the normal to this plane would still be an axis of optical symmetry. Ramanathan* has discussed the explanation of the optical anisotropy of the benzene molecule and given very good reasons for the belief that there is an optical axis of symmetry, and that the optical moment induced by the field of a light-wave in a direction parallel to this axis is considerably smaller than in directions perpendicular to it. If we combine this with the idea suggested by the case of graphite, that the diamagnetic susceptibility is numerically greater along this line than in perpendicular directions, we get a positive value for the Cotton-Mouton constant, as actually observed. The existence of an axis of optical symmetry makes $A = B$. The expressions for C_m and δ then reduce to

$$C_m = -\frac{(n_0^2 - 1)(n_0^2 + 2)}{60n_0\lambda kT} \cdot \frac{A - C}{2A + C} [3C' - (A' + B' + C')] \quad (8)$$

and

$$\delta = 2 \left(\frac{A - C}{2A + C} \right)^2. \quad (9)$$

Now $A' + B' + C'$ is a constant proportional to the total susceptibility $= \theta$, say. Then C_m can be written in the form

$$C_m = -\frac{(n_0^2 - 1)(n_0^2 + 2)}{60n_0\lambda kT} \cdot (3C' - \theta) \sqrt{\frac{\delta}{2}}. \quad (10)$$

We can easily compute the values of the Cotton-Mouton constant corresponding to different values for the ratio C'/θ . If $C' = \theta$, then the entire magnetic susceptibility of benzene is concentrated in one direction only; in other words, it is magnetisable only along the axis of optical symmetry. The ratio C'/θ thus represents the fraction of the total magnetic susceptibility concentrated along this axis. In row 2 of Table II the theoretical value of the Cotton-Mouton constant for different values of the ratio C'/θ is shown, the value of δ being derived from formula (5). In row 3 of Table II the theoretical values of the Cotton-Mouton constant are shown similarly, δ being derived from formula (6). The observed value of the Cotton-Mouton constant $= 5.90 \times 10^{-13}$. A comparison of this value with those shown in the table indicates that according to either method of calculation we have to assume that a considerable proportion of the magnetic susceptibility of benzene is concentrated in one direction, in order that the observed and calculated values of the Cotton-Mouton constant might agree. According to row 2 we should find the ratio of

* K. R. Ramanathan, 'Roy. Soc. Proc.,' A, vol. 110, p. 123 (1926).

the susceptibility along the principal axis to that in perpendicular directions to be 17 : 10, while according to row 3 the ratio is 21 : 10.

Table II.—Observed Value of the Cotton-Mouton Constant = 5.90×10^{-13} .

		0.60	0.55	0.50	0.45	0.40	0.333
Cotton-Mouton constant calculated from—	formula (5) $\times 10^{13}$	12.6	10.2	7.85	5.49	3.14	0
	formula (6) $\times 10^{13}$	8.88	7.21	5.55	3.89	2.22	0

6. Interpretation of the Observed Results.

The remarkable magnetic anisotropy of the benzene ring indicated by the foregoing investigation demands an explanation. In the entire structure of the molecule we have 42 electrons in all outside the atomic nuclei. Of these, 12 electrons belong to the K rings of carbon, and the size of their orbits is so small that they cannot contribute appreciably to the diamagnetic susceptibility of the molecule. We are thus left with 30 electrons which contribute to magnetic susceptibility and can or may take part in the chemical binding of the atoms. Pauling* has recently suggested a plane structure for the benzene ring in which 12 electrons are held in pairs in orbits binding the carbon and hydrogen atoms, 12 electrons in pairs connect the neighbouring carbon atoms, and the 6 remaining electrons form three pairs which connect each carbon atom with the one opposite to it directly across the ring. This structure would make the molecule diamagnetic. If we make the further assumption that at least 12 of the electron orbits are in the plane of the ring, we would have an explanation of the observed magnetic anisotropy of the molecule. If, on the other hand, the molecule is not a plane structure but is a puckered ring, an even larger proportion of the orbits may be orientated in planes approximately parallel to the ring consistently with its observed magnetic anisotropy.

7. Some Benzene Derivatives.

When one or more of the hydrogen atoms in benzene is replaced by other atoms or groups, we shall no longer be justified in taking the optical ellipsoid of the molecule to be a spheroid of revolution. If, however, the replacing atoms or groups are not themselves strongly anisotropic optically, we may, as a rough approximation, assume the derivative to have an optical axis of symmetry and

* L. Pauling, 'Jour. Am. Chem. Soc.,' vol. 48, p. 1139 (1926).

calculate the magnetic anisotropy of the molecule in the same way as was done in the case of benzene. Instead of following the latter procedure, however, it would perhaps be of greater interest to attempt to calculate the Cotton-Mouton constant for these derivatives, assuming that the atoms or groups which replace the hydrogen to be magnetically isotropic, and leave the magnetic anisotropy of the rest of the benzene ring unaffected. Let us take, for example, ethyl benzene ($C_6H_5 \cdot C_2H_5$). It has already been mentioned that the aliphatic hydrocarbons exhibit a much smaller magnetic anisotropy, if any, than the aromatics. Hence to a first approximation we may assume that the contribution from the ethyl radical to the magnetic susceptibility of the molecule would be the same along the three optic axes. If, also, the contribution from the benzene ring to the susceptibilities along these axes be supposed to be unaffected, it will easily be seen that the factor $(3C' - \theta)$ in expression (10) will remain unaltered, since the increase in C' will be a third of the increase in θ . Thus the expression for the Cotton-Mouton constant reduces to

$$C_m = \text{constant} \times \frac{(n_0^2 - 1)(n_0^2 + 2)}{n_0} \sqrt{\delta}. \quad (11)$$

The constant can be evaluated from the observed value of C_m for benzene, and will be different according as we use formula (5) or (6) for calculating δ . The values of the Cotton-Mouton constant so calculated are given in Table III. The

Table III.

Liquid.	De-polarisation factor $\times 100$.	Refractive index for 0.578μ	Susceptibility per gram molecule $\times 10^6$	$\delta \times 10^3$		Cotton-Mouton constant $\times 10^{13}$.		
				from formula (5)	from formula (6)	Calculated		Observed.
						using δ from formula (5)	using δ from formula (6)	
Benzene	47	1.505	5.74	90	45	5.9	5.9	5.90
Toluene	51	1.499	6.99	86	43	5.7	5.7	6.20
Ethyl benzene	53	1.498	8.20	78	39	5.4	5.4	5.44
<i>m</i> -Xylene	57	1.501	8.21	95	48	6.0	6.0	6.33
<i>p</i> -Xylene	58	1.498	8.21	103	52	6.2	6.2	6.83
Chlorobenzene	58	1.528	7.52	111	53	6.9	6.8	7.29
Bromobenzene	63.5	1.563	8.62	137	63	8.3	8.0	6.50
Aniline	60	1.589	6.51	92	40	7.2	6.7	4.03
Benzyl chloride	56	1.542	8.76	78	37	6.0	5.8	6.12
Benzal chloride	52	1.568	10.55	57	26	5.4	5.2	6.02

air agreement between the calculated and observed values shows that in all these cases, except perhaps those of aniline and bromobenzene, our assumptions are not far from the truth.

8. *Summary.*

The paper contains a discussion of the magnetic double-refraction exhibited by liquid benzene and some of its derivatives on the basis of the Langevin theory, utilising the data for optical anisotropy of the molecules derived from observations on light-scattering. The following is a summary of the results obtained :—

(1) A comparison of magnetic double-refraction and light-scattering by hexane, cyclohexane and benzene shows that the differences between the aromatic and the aliphatic hydrocarbons in respect of magnetic anisotropy must be even more pronounced than their differences in respect of their optical anisotropy.

(2) Making the justifiable assumption that the optical ellipsoid of the benzene molecule is an oblate spheroid of revolution, it is shown that the observed value of the Cotton-Mouton constant can only be explained on the assumption that the molecule exhibits a very pronounced magnetic anisotropy, the susceptibility in the direction of the axis being about twice as large as in perpendicular directions.

(3) As an explanation of this result, it is suggested that at least 12 of the electron orbits binding the atoms in the molecules must be orientated in a plane parallel to the ring.

(4) The absolute value of the Cotton-Mouton constant has been calculated for some of the simpler benzene derivatives in which it can be assumed without serious error that the optical ellipsoid is still a spheroid of revolution, and that the group which replaces the hydrogen atom is magnetically isotropic. The calculated and observed values are in fair agreement.
