OPTIC MOMENTS OF ORGANIC MOLECULES IN RELATION TO CRYSTALLINE AND MAGNETIC BIREFRINGENCE.

BY M. RAMANADHAM

(From the Department of Physics, Andhra University, Waltair.)

Received August 10, 1935.
(Communicated by Mr. S Bhagavantam)

1. Introduction.

In a previous communication (Ramanadham, 1934), the author had shown how the principal refractive indices of a crystal could be correlated with the principal optic moments of the molecules constituting it and their orientation inside. As a particular case, the optic moments of the naphthalene molecule were deduced on the one hand from the known (1) refractive index, (2) the magnetic birefringence of the substance in the liquid state, and (3) the depolarisation of the light scattered by its vapour, and on the other hand from the observed principal refractive indices of the crystal together with the known orientations of the molecules. Agreement was found to be fair between the sets of optic moments deduced by these two entirely different methods.

It appears desirable to extend this treatment to a number of other organic crystals. As a preliminary to it, has been here undertaken the determination of the magnetic birefringence of organic solids in solution with carbon tetrachloride as the solvent. The choice of the solvent is based on the fact that carbon tetrachloride is known to exhibit no detectable magnetic double refraction. The substances are specially chosen from among those whose magnecrystalline behaviour has been studied by Krishnan.

2. Experimental.

The experimental arrangement is the same as that adopted in the author's previous investigations (Ramanadham, 1929). The method of estimation of the positive double refraction exhibited by the aromatic compounds is, however, slightly different in the present arrangement. Instead of compensating the double refraction by compressing a plate horizontally, the compensation is now made more conveniently by elongating a glass plate vertically by weights hung from it. All the measurements are made with respect to benzene and the absolute values calculated by assuming the value of $C_M$ for benzene as $5 \times 10^{-13}$ at 30° C.
To prepare solutions of definite concentration, a measuring flask of 25 c.c. capacity, provided with a ground-glass stopper, is taken and into it is put a weighed quantity of the substance under investigation. Then carbon tetrachloride liquid is run down from a burette into the flask and after dissolving the substance, the volume of the solution is made up to 25 c.c. by further running down the required amount of CCl₄. At the same time, the total volume of CCl₄ run down is noted.

As the refractive indices of the solutions are required in the calculations, they have been determined with an Abbe refractometer.

3. Results.

The results are exhibited in the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature</th>
<th>Weight of the substance in 25 c.c. of the solution</th>
<th>Volume of CCl₄ in 25 c.c. of the solution</th>
<th>Refractive index of the solution for the D line</th>
<th>CΜ × 10⁻¹¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>27°-5 C.</td>
<td>2.5 g.</td>
<td>22.5 c.c.</td>
<td>1.4729</td>
<td>3.1</td>
</tr>
<tr>
<td>&quot;</td>
<td>27°-5 C.</td>
<td>4.0 &quot;</td>
<td>20.8 &quot;</td>
<td>1.4834</td>
<td>4.6</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>30° C.</td>
<td>8.0 &quot;</td>
<td>17.5 &quot;</td>
<td>1.5084</td>
<td>4.0</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>30° C.</td>
<td>3.0 &quot;</td>
<td>22.2 &quot;</td>
<td>1.4770</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzil</td>
<td>32° C.</td>
<td>2.9 &quot;</td>
<td>22.5 &quot;</td>
<td>1.4728</td>
<td>1.5</td>
</tr>
<tr>
<td>Salol</td>
<td>32° C.</td>
<td>7.0 &quot;</td>
<td>19.4 &quot;</td>
<td>1.4910</td>
<td>2.1</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>29° C.</td>
<td>7.0 &quot;</td>
<td>19.1 &quot;</td>
<td>1.4990</td>
<td>2.1</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>31° C.</td>
<td>2.5 &quot;</td>
<td>22.9 &quot;</td>
<td>1.4822</td>
<td>3.1</td>
</tr>
</tbody>
</table>

4. Discussion.

(a) Naphthalene.—It is desired to see how far the observed values of CΜ in the case of naphthalene solutions agree with those obtained by Salceanu (1932) in molten naphthalene. In calculating the magnetic birefringence to be expected for naphthalene solutions, we will accordingly make use of the optic moments \( b_1 = 25.85 \times 10^{-24}, \ b_2 = 22.25 \times 10^{-24} \) and \( b_3 = 9 \times 10^{-24} \) derived by the author in an earlier paper (loc. cit.) on the basis of Salceanu’s value of CΜ for molten naphthalene.

Applying the formula*

\[
C_\mu = \frac{1}{20} \cdot \frac{n^2 - 1}{n \hbar k T} \cdot \frac{v_1[(a_1 - a_2)(B_1 - B_2) + \cdots] + v_2[(a_1' - a_3')(B_1' - B_3') + \cdots]}{v_1(b_1 + b_2 + b_3) + v_2(b_1' + b_2' + b_3')}
\]

the values of $C_M$ for naphthalene solutions at the two concentrations for which observations have been made are calculated and shown below:

<table>
<thead>
<tr>
<th>Wt. of the naphthalene in 25 c.c. of the solution</th>
<th>Observed $C_M \times 10^{13}$</th>
<th>Calculated $C_M \times 10^{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2·5 g.</td>
<td>3.1</td>
<td>2.5</td>
</tr>
<tr>
<td>4·0 ,,</td>
<td>4.6</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The agreement between the observed and calculated values is fair within the degree of experimental error. In making the calculation, it is assumed that the carbon tetrachloride molecule is optically and magnetically isotropic, that the second term in the numerator vanishes, and that the second term in the denominator becomes $n^2 3b'$ where $b'$ is the optic moment of the carbon tetrachloride molecule in the gaseous condition; this can be deduced from the known refractive index of the liquid at the known density by applying Lorentz’s equation

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{3}{4\pi} = b'.$$

The values of $B_1$, $B_2$, $B_3$ are obtained from equations of the form $B_1 = b_1(1 + p_1 x)$, where $x$ is the optical susceptibility of the solution. The values of $p_1$, $p_2$ and $p_3$ are the same as those used previously, namely, 1·8, 2·8 and 8·0.

(b) Diphenyl.—From a study of the magnetic anisotropy of the crystal, Krishnan (1933) has been led to place the length of the molecule at an angle 20°·1 from the C axis and the breadth in the plane of the molecule at 31° to the $b$ axis. This orientation has been confirmed by Dhar (1932) by X-ray analysis.

The refractive indices of the crystal are given by Narasimham (1931) as 1·554, 1·586 and 1·647. He has also given certain data regarding the disposition of the principal axes of the optical ellipsoid and the optic axes but these are not consistent amongst themselves. Hendricks and Jefferson (1933) who subsequently repeated the measurements on the crystal found the refractive indices to be 1·5598, 1·6542 and >1·90. These authors do not, however, give any information regarding the disposition of the principal optic axes with reference to the crystallographic axes. Groth has recorded that the optic axes make 20°·75 and 57°·75 respectively with the normal to the 001
face where the interference figure is viewed through cedar oil (Refractive index 1.515).

An attempt is made in the present investigation to decide between the conflicting results regarding the refractive indices and to fix the directions of the principal axes of the optical ellipsoid by making the following observations.

The apparent angle made by one of the optic axes with the normal to the plate is measured as 31°·8 by mounting the crystal on a Fedorov stage under the microscope and tilting it until the corresponding melatope coincides with the intersection of the crosswires. This reading is in agreement with the angle 20°·75 given by Groth if we take into account the fact that the latter has been measured under cedar oil of refractive index 1.515.

It is further noticed that the interference figure shown by a diphenyl crystal of thickness 0.109 mm. between crossed nicols exhibits 13 complete rings. The double-refraction in the plate, i.e., in 001 plane becomes then 0.0701.

To see which set of refractive indices gives this observed double refraction 0.0701 in the (001) plane, the true angles made by the optic axes with the normal are calculated with the aid of each one of the alternative values available for the intermediate refractive index, assuming the apparent angles given by Groth as correct and then the birefringence in the plate from both sets of values† by applying the formula

\[
\frac{1}{a'^2} - \frac{1}{\gamma'^2} = \left(\frac{1}{a^2} - \frac{1}{\gamma^2}\right) \cdot \sin \theta \cdot \sin \theta'
\]

where \(a'\) and \(\gamma'\) denote the principal indices in the plate the normal to which makes the real angles \(\theta\) and \(\theta'\) with the optic axes and \(a\) and \(\gamma\) denote the minimum and maximum principal refractive indices of the crystal.

\(a' - \gamma'\) has come out according to Narasimham's set of values as 0.024 and according to those of Hendricks and Jefferson as 0.0712. The latter is in satisfactory agreement with the author's observations and hence Hendricks and Jefferson's values are taken as reliable.

We proceed now to fix the orientations of the principal optic axes. The true angles \(\theta\) and \(\theta'\) are (from Hendricks and Jefferson's refractive indices and Groth's apparent angles) 18°·56' and 50°·48'. Hence the acute bisectrix which in this case is the direction of maximum refractive index can easily be seen with the aid of the figure to make an angle of 20°·42' with the crystallographic C axis in the obtuse angle.

† In the case of values given by Hendricks and Jefferson the maximum refractive index is put equal to 1.90.
This indeed coincides with the minimum diamagnetic axis and hence the direction in which the length of the molecule lies. Thus it appears that the optics of a suitable monoclinic crystal will enable us to fix the direction of the length of the molecule along which we naturally expect the maximum optical polarisability to occur. Unfortunately the data on the optics of organic crystals are very meagre and where available not quite reliable and so we cannot extend such investigations to other cases.

We now calculate the optic moments $b_1$, $b_2$ and $b_3$ of the diphenyl molecule from the known orientations which are represented in the scheme below and by making use of the formula which the author has derived in the previous paper (loc. cit.) for the refractive indices in the principal directions. The values of $p_1$, $p_2$ and $p_3$ are assumed to be 1.8, 2.8 and 8.0 same as those of naphthalene to which assumption we have been led by comparing the dimensions of the unit cell and the angle $\beta$ in both cases. The density of the crystal is 1.154 (Ashutosh Mukherjee, 1933)

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>2</td>
<td>90°</td>
<td>31°</td>
<td>59°</td>
</tr>
<tr>
<td>3</td>
<td>90°</td>
<td>59°</td>
<td>31°</td>
</tr>
</tbody>
</table>

$X$, $Y$, $Z$ are respectively the directions of maximum, intermediate and minimum refractive indices. 1, 2, 3 represent respectively the directions of the length, breadth and thickness of the molecule which are mutually at right
angles to one another. \( b_1 = 33.32 \times 10^{-24} \), \( b_2 = 23.06 \times 10^{-24} \), \( b_3 = 12.13 \times 10^{-24} \) c.g.s. units. From Krishnan, we have for the diamagnetic moments \( a_1 = -1.1039 \times 10^{-28} \), \( a_2 = -1.1039 \times 10^{-28} \) and \( a_3 = -2.8828 \times 10^{-28} \) c.g.s. units.

Substituting these values in the formula for \( C_M \) for the concentration for which observations have been made, the calculated value of \( C_M \) comes out as \( 4.3 \times 10^{-13} \) against the observed value \( 4.0 \times 10^{-13} \) in very close agreement.

The refractive index of the solution can also be calculated by the aid of the formula

\[
\frac{n^2 - 1}{4\pi} = \frac{v_1(b_1 + b_2 + b_3) + v_2(b_1' + b_2' + b_3')}{1 - \frac{1}{3}v_1(b_1p_1 + b_2p_2 + b_3p_3) - \frac{1}{3}v_2(b_1'p_1' + b_2'p_2' + b_3'p_3')} \]

which takes into account the anisotropy of the optical polarisation field. The calculated value comes out as 1.522 which is in fair agreement with the observed value 1.5084.

(c) Dibenzyl.—The magnetic birefringence of this substance has not been studied by the author as it was not available. We can, however, make use of the available data to discuss this case.

The refractive indices of the crystal have been given by Hendricks and Jefferson as 1.7566, 1.6286 and 1.5292. The density of the crystal is 1.0738. The dimensions of the molecule are taken as 11, 11 and 3.8 A.U.; for which the values of \( p_1, p_2, p_3 \) are calculated in the usual manner.

\[ p_1 = p_2 = 2.579 \text{ and } p_3 = 7.877. \]

Groth’s qualitative observations show that the direction of maximum refractive index lies at almost the same direction as the length of the molecule which Krishnan has fixed at an angle of 83°·9 to the C axis. By analogy with diphenyl, we make the assumption that it coincides with the direction

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>2</td>
<td>90°</td>
<td>30°</td>
<td>60°</td>
</tr>
<tr>
<td>3</td>
<td>90°</td>
<td>60°</td>
<td>30°</td>
</tr>
</tbody>
</table>

Optic Moments of Organic Molecules in Relation to Birefringence

of the length, and since $b$ axis is by virtue of symmetry also the axis of intermediate refractive index, the principal directions of the crystal are easily fixed. The above is the scheme of orientations of the principal axes 1, 2, 3 of the molecule with respect to them.

The values of $b_1$, $b_2$, $b_3$ calculated come out as $b_1 = 32.36 \times 10^{-24}$, $b_2 = 28.74 \times 10^{-24}$ and $b_3 = 14.36 \times 10^{-24}$ c.g.s. units.

The observed refractive index of the liquid dibenzyl at a density of 0.942 grams per c.c. is given as 1.539 (I.C.T., Vol. I) which compares very favourably with 1.535 calculated from the formula

$$n^2 - 1 = \frac{B_1 + B_2 + B_3}{3}$$

where

$$B_1 = b_1 \left( 1 + \rho_1 \frac{n^2 - 1}{4\pi} \right).$$

Though this test on the optic moments is not unique, yet a comparison of these values with those of diphenyl shows that they are reliable.

5. Conclusion.

In conclusion we point out that the results obtained in the case of diphenyl are significant, showing how the optical properties of a crystal can be a useful check on the X-ray or magnetic analysis of molecular orientation when combined with the knowledge of the magnetic double-refraction, refractivity and depolarisation of the scattered light. At the same time, the validity of the various theories is put to the test. For instance, the theory of magnetic birefringence in regarding it as arising out of the orientation of optically and magnetically anisotropic molecules has found a direct verification in the phenomenon being connected with other independent phenomena, namely, the optical and magnetic anisotropy of crystals. Also the idea of anisotropic polarisation field has consistently been employed. The author's molecular theory of double-refraction of organic crystals has also been put to the test.

The author is highly thankful to Prof. Sir C. V. Raman, Kt., M.A., D.Sc., F.R.S., N.L., for having allowed the use of the strong electromagnet at the Indian Institute of Science, Bangalore, for making some of the observations contained in the present paper. He is also thankful to Mr. S. Bhagavantam for the many useful discussions which the author had with him on the subject. He takes this opportunity also to thank the syndicate of the Andhra University for having awarded him a Research Fellowship at the beginning of this academic year.
The results of observations made on the magnetic birefringence of organic solids dissolved in liquid carbon tetrachloride are given. The observed values of $C_M$ for naphthalene solutions are compared with the value of $C_M$ observed by Salceanu on molten naphthalene and found to be in good agreement. The principal optic axes of the diphenyl crystal are fixed on the basis of the author's own observations, those of Groth and also of Hendricks and Jefferson. The direction of maximum refractive index has been found to coincide with the direction which has been assigned to that of the length of the molecule by Krishnan from his diamagnetic observations on the crystal. The optic moments of diphenyl molecule are calculated from the refractive indices and are found to satisfy the observed magnetic birefringence and the refractive index of the solution. The optic moments of the dibenzyl molecule are similarly calculated from the refractive indices and found to agree with the observed refractive index of the liquid dibenzyl.

REFERENCES.