The Structure of Molecules in Relation to their Optical Anisotropy.—Part II—Benzene and Cyclohexane.

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1. *Introduction.*

In Part I* the view was advanced that the optical anisotropy of the molecules of a gas which is evidenced by the depolarisation of the light scattered by it can to a large extent be attributed to the mutual influence of the doublets induced in the different atoms of the molecule by the electrical field of the incident radiation.

Assuming that each atom is isotropic, and assuming the refractivity and anisotropy of the molecules of hydrogen, oxygen and nitrogen, the atomic refractivity and the distance apart between the " optical centres " was calculated in these cases. Extending the treatment to the case of triatomic molecules with the three atoms in a straight line, and using the previously obtained values for the atomic refractivities of nitrogen and oxygen and the diamond value of the atomic refractivity of carbon, the optical anistropies of the gases N_2O, CO_2 and CS_2 were calculated. The corresponding values of the depolarisation of the transversely scattered light were found to be in fair agreement with experiment. In this paper the work is extended to the two organic molecules, benzene and cyclohexane.

2. *Polarisation of the Scattered Light in Benzene and Cyclohexane.*

The imperfection of polarisation of the transversely scattered light in benzene vapour has been recently measured by Raman and Rao† and by Ganesan.‡ Their values are 0·068 and 0·066 respectively. We shall adopt the average of these two values, 0·067. Ganesan has also made measurements on a few benzene derivatives with the following results :—

Toluene	0·064
m-Xylene	0·067
Chloro-Benzene	0·078
Bromo-benzene	0·078

* 'Roy. Soc. Proc.,' A, vol. 107, p. 684.
† 'Phil. Mag.,' vol. 46, p. 426 (1923).
‡ 'Phil. Mag.,' vol. 49, p. 1216 (1925).

It is significant that the values do not differ much from each other, which shows that the major part of the anisotropy has its origin in the benzene structure.

No previous measurements on the depolarisation of the light scattered by cyclohexane vapour have been recorded. The author has recently measured its value, using sunlight for illumination, and found it to be 0·011. A simple glass apparatus was employed for the measurement, and as the apparatus has been found particularly convenient for work with vapours which require heating, and as only small quantities of the substances are required, it may be worth while to describe it briefly.

Two bulbs, A and B, were blown on a tube of clear glass of about 2 cm. internal diameter, particular care being taken to see that there were no streaks or uneven portions on the bottom of the bulb B. The purpose of the second bulb is to prevent light diffused from places on the walls of the first bulb A which are struck by the incident light from reaching the observing window. The stem of the tube was about 20 cm. in length, and its end was drawn out into a horn (fig. 1). After cleaning and drying, a small quantity of the pure liquid was introduced into the bulb, and after evacuation with a pump, the tube was sealed off. The bulb was painted over with black paint, except for two windows in A for the entry and exit of a narrow pencil of sunlight and a small rectangular window in the bottom of B for observation. The tube was mounted horizontally inside a big iron cross-tube blackened inside and provided with suitable diaphragms to shut out stray light, and the measurements of the depolarisation were made visually with a double image prism and nicol. Arrangements were made to heat up the tube to different temperatures by means of an electric current. When the measurements are made with a view to obtain the optical anisotropy of the molecule, it is important to keep the density of the vapour as low as possible. The temperature was usually kept below the boiling point of the liquid. Check measurements on the vapours of benzene and carbon disulphide gave values 0·066 and 0·143 against Ganesan's values 0·066 and 0·167.
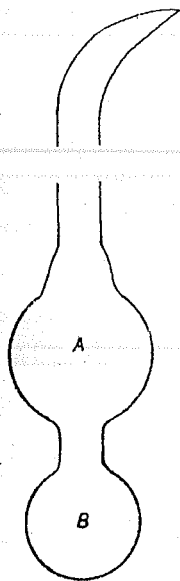

Fig. 1.

3. *Calculation of the Optical Anisotropy of Benzene.*

If A, B, C be the polarisations induced in a molecule when its three principal directions are respectively along the direction of an electric field of unit intensity

and of the frequency of the incident radiation, then the ratio of the weak component to the strong in the light scattered perpendicular to the incident beam is[*]

$$r = \frac{2(A^2 + B^2 + C^2) - 2(AB + BC + CA)}{4(A^2 + B^2 + C^2) + AB + BC + CA} \qquad (1)$$

In the particular case when $A = B$, this becomes

$$r = \frac{2(A - C)^2}{9A^2 + 4C^2 + 2AC}.$$

In order to calculate the values of A, B and C for any molecule, it is necessary to assume some structure for it. In the case of benzene, chemical evidence requires that the six carbon atoms and the six hydrogen atoms are similar. From the further negative evidence that no optically-active derivative of benzene containing a single nucleus has been isolated, it has been held that the six carbon atoms lie in the same plane at the angular points of a regular hexagon,[†] and that the hydrogen atoms lie in the same plane at the six corners. On the other hand, if we proceed from the analogy of the crystal structures of naphthalene and anthracene as analysed by Sir W. H. Bragg,[‡] the carbon atoms would be arranged in a puckered hexagonal ring as in diamond, the hydrogen atoms being joined to the carbons at the tetrahedral angle.

In order to decide which of these structures to adopt, a preliminary calculation was made in which the hydrogen atoms were ignored. The anisotropy of a structure consisting of six carbon atoms was calculated both when they are arranged in a plane ring as in graphite, and when they are arranged in a puckered ring as in diamond. In the former case, the distance between the centres of two neighbouring carbon atoms was assumed to be 1·45 A.U. and in the latter case 1·50 A.U. Calculations were made for two values of the atomic refractivity, viz., (1) the refractivity of carbon in diamond and (2) the refractivity usually ascribed to carbon in organic compounds.

The three principal directions in the molecule were taken to be (1) OX, parallel to 1–3 in fig. 2 ; (2) OY, perpendicular to 1–3 in the plane of the paper ; and (3) OZ, perpendicular both to 1–3 and to the plane of the paper. In the case of the puckered ring structure, the atom-centres 1, 3, 5 lie in the plane of the paper, while 2, 4, 6 lie 0·5 A.U. above this plane.

[*] Lord Rayleigh, 'Phil. Mag.,' vol. 35, p. 373 (1918).
[†] J. F. Thorpe, 'Chemistry in the Twentieth Century.'
[‡] W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' chap. XIV.

I. *Plane Ring of Six Carbon Atoms.*—When the field is parallel to the X-axis, the resultant electric intensity at each atom will be confined to the XY plane. The X-components of the polarisations of 1, 3, 4 and 6 will, by symmetry, be the same (fig. 3), say ex_1, and those of the atoms 2 and 5 will
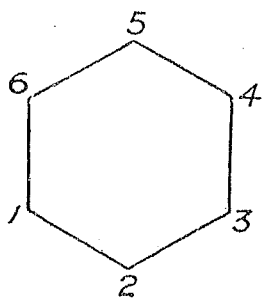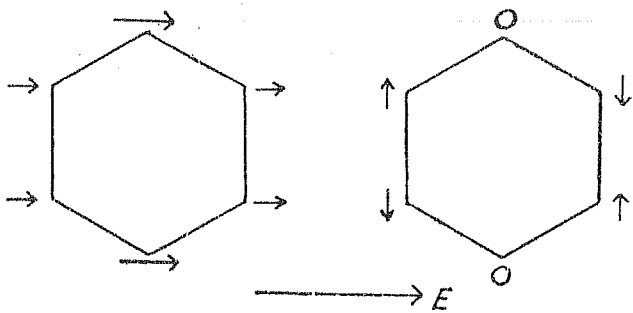

Fig. 2.   Fig. 3.

also be the same but have a different value, say ex_2. The y components of 2 and 5 will vanish, while those at 1, 3, 4 and 6 will be equal to each other, but alternate in sign.

The x-component of the electric intensity at any atom will be given by

$$E' = E + \Sigma \frac{3a^2 - r^2}{r^5} ex_n + \Sigma \frac{3ab}{r^5} . ey_n + \Sigma \frac{3ac}{r^5} ez_n, \qquad (2)$$

where E is the electric vector in the incident light ex_n, ey_n, ez_n are the components of the polarisation of any other atom in the molecule whose co-ordinates with respect to the atom we are considering are a, b, c, and r is the distance between the two atoms. The summation is extended to all the other atoms in the molecule.

The polarisation due to this field is given by

$$ex = e^2 \lambda E'$$

where $e^2 \lambda$ is obtained from Lorentz's equation for the atomic refractivity

$$\frac{A}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_0 e^2 \lambda.$$

A is the atomic weight of the element, ρ is its density, n its refractive index, and N_0 the number of molecules in a gram-molecule.

Taking the atomic refractivity of diamond to be 2·124,* we get the value of $e^2 \lambda$ for carbon to be $0·836 \times 10^{-24}$, and calculating the field due to the other atoms, and summing them up with their proper signs, we obtain

* Part I.

$$1 \cdot 196 \, ex_1 = \text{E} \times 10^{-24} - 0 \cdot 151 \, ex_1 + 0 \cdot 394 \, ex_2 - 0 \cdot 0533 \, ey_1$$

$$1 \cdot 196 \, ex_2 = \text{E} \times 10^{-24} + 0 \cdot 788 \, ex_1 - 0 \cdot 041 \, ex_2 - 0 \cdot 688 \, ey_1$$

$$1 \cdot 196 \, ey_1 = \qquad\qquad 0 \cdot 053 \, ex_1 - 0 \cdot 344 \, ex_2 - 0 \cdot 603 \, ey_1.$$

Solving, we get

$$ex_1 = 1 \cdot 25 \, \text{E} \times 10^{-24}$$

$$ex_2 = 1 \cdot 77 \, \text{E} \times 10^{-24}$$

$$ey_1 = - \, 0 \cdot 30 \, \text{E} \times 10^{-24}.$$

The total polarisation parallel to the inducing field is $4ex_1 + 2ex_2$, which is equal to $8 \cdot 54 \, \text{E} \times 10^{-24}$.

When the field is parallel to OY, the same value of the polarisation is obtained. The molecule is thus isotropic in the XY plane.

When the field is parallel to OZ, the fields at any atom due to the other atoms oppose each other, thus producing a weaker resultant field and hence a smaller polarisation. Calculating as before, the induced moment of each atom in this case comes out to be $0 \cdot 495 \, \text{E} \times 10^{-24}$, and hence the total for the six atoms is $2 \cdot 97 \, \text{E} \times 10^{-24}$.

The optical anisotropy is thus A : B : C $= 8 \cdot 54 : 8 \cdot 54 : 2 \cdot 97 = 2 \cdot 94 : 2 \cdot 94 : 1$, and the imperfection of polarisation of the transversely scattered light calculated according to (1) is $0 \cdot 083$.

If the refractivity of carbon is assumed to be that usually adopted in tables of refractivities, namely, $2 \cdot 44$ (for the F line), the polarisations parallel to the field when the field is along the X and Z axes respectively are found to be

$$\left. \begin{array}{l} ex_1 = 1 \cdot 58 \, \text{E} \times 10^{-24} \\ ex_2 = 2 \cdot 34 \, \text{E} \times 10^{-24} \end{array} \right\}$$

and

$$ez_1 = 0 \cdot 534 \, \text{E} \times 10^{-24}$$

leading to a value of the anisotropy $3 \cdot 4 : 3 \cdot 4 : 1$ and a depolarisation of the transversely scattered light of $0 \cdot 10$.

II. *Puckered Ring of Six Carbon Atoms.*—Assumed distance between the centres of two neighbouring carbon atoms $= 1 \cdot 50$ A.U. Assumed atomic refractivity of carbon $= 2 \cdot 124$.

Starting from the atom on the left-hand bottom corner, the co-ordinates of the centres of the different atoms are given below (see Table I).

TABLE 1.

	a.	b.	c.
1	0	0	0
2	1·225	−0·707	0·500
3	2·450	0	0
4	2·450	1·414	0·500
5	1·225	2·121	0
6	0	1·414	0·500

When the electric vector in the incident light is parallel to the X-axis, the directions of the X- and Y-components of polarisation will be as in figure 3, but
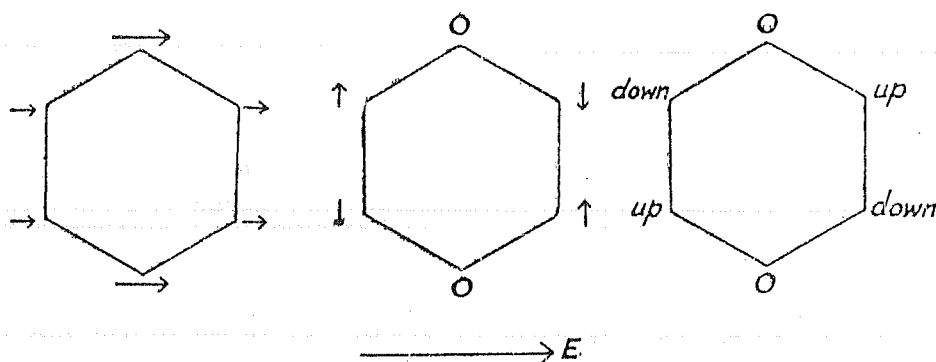

FIG. 4.

since the atoms are not confined to the XY-plane, the Z-components will not vanish. They will be as shown in fig. 4. We have therefore four unknowns to determine, namely, ex_1, ex_2, ey_1 and ez_1. The appropriate equations are found to be

$$1 \cdot 196\, ex_1 = E \times 10^{-24} - 0 \cdot 110\, ez_1 + 0 \cdot 279 ex_2 + 0 \cdot 053 ey_1 + 0 \cdot 018 ez_1$$
$$1 \cdot 196 ex_2 = E \times 10^{-24} + 0 \cdot 559 ex_1 - 0 \cdot 042 ex_2 - 0 \cdot 507 ey_1 + 0 \cdot 484 ez_1$$
$$1 \cdot 196 ey_1 = 0 \cdot 053 ex_1 - 0 \cdot 254 ex_2 - 0 \cdot 438 ey_1 - 0 \cdot 269 ez_1$$
$$1 \cdot 196 ez_1 = 0 \cdot 019 ex_1 + 0 \cdot 242 ex_2 - 0 \cdot 268 ey_1 + 0 \cdot 227 ez_1$$

which when solved give

$$ex_1 = 1 \cdot 11\, E \times 10^{-24}$$
$$ex_2 = 1 \cdot 63\, E \times 10^{-24}$$
$$ey_1 = - 0 \cdot 301\, E \times 10^{-24}$$
$$ez_1 = 0 \cdot 512\, E \times 10^{-24}$$

The resultant polarisation is along the direction of the field and is given by $4ex_1 + 2ex_2 = 7 \cdot 70\, E \times 10^{-24}$.

Writing down the appropriate equations when the incident field is parallel to the Z-axis and solving, we get for the total polarization parallel to the Z-axis $3 \cdot 68 \, E \times 10^{-24}$. The resultant polarizations in other directions vanish.

The calculated value of r is $0 \cdot 050$.

If we take the atomic refractivity of carbon to be $2 \cdot 44$, we get $A : B : C = 10 \cdot 0 : 10 \cdot 0 : 4 \cdot 14$ and $r = 0 \cdot 065$.

III. *Puckered Ring of Six Carbon Atoms with the Hydrogens introduced.*—In the calculations made above, we have altogether ignored the effect of the hydrogen atoms. Their introduction either in the plane of the carbon atoms in Case I or in the appropriate positions in the approximate plane of the puckered ring in Case II can only lead to an increase in the anisotropy. We have already found that if we adopt the plane ring structure, the calculated value of the anisotropy is too high even with the smaller value of the atomic refractivity. Unless therefore we assume that the distance between the optical centres is greater than $1 \cdot 45$ A.U., or that the atoms themselves are distinctly anisotropic with their axis of larger polarization perpendicular to the plane of the ring, we cannot explain the observed anisotropy of benzene with this structure. Since, however, the carbons are bounded on the outside by the hydrogens, it is unlikely that the distance between the optical centres of the carbons is really much greater than the X-ray distances. As for the second alternative, although it is quite likely that in a graphite structure, the atoms are more polarizable perpendicular to the plane than parallel to the plane, since we have nothing definite to go by, it is better for the present not to bring in an unknown factor in the shape of the anisotropy of the individual carbon atom. We shall therefore in what follows adopt the puckered ring structure of the carbon and work out the effect of introducing the hydrogens.

The question of the position of the hydrogen atoms is a difficult one. We shall assume that each hydrogen is joined to its carbon at the tetrahedral angle, the projection of the whole structure upon the average plane of the ring being the familiar graphic formula for benzene. In order to calculate the distance of a hydrogen atom from the centre of a neighbouring carbon atom, we cannot adopt the usual X-ray "diameter" of hydrogen, as in this case the hydrogen is not bounded by other atoms on the outside. In Part I, it was calculated that the distance between the optical centres in a hydrogen molecule is $1 \cdot 37$ A.U. Adding half this distance to the "radius" of a carbon atom, we obtain $1 \cdot 43$ A.U. to be the required distance. The atomic refractivity of hydrogen is assumed to be that calculated in Part I and the refractivity of carbon to be that of diamond.

The calculations were made exactly on the same lines as before, but since we have now to deal with the polarizations of twice as many atoms, we have twice as many unknowns. The appropriate equations for the polarizations of the different atoms were written down, and their solution was obtained by a method of successive approximations. Assuming the values of the polarization of the carbon atoms obtained above when the hydrogens were not present, the polarizations of the hydrogens were calculated neglecting the small influence of the other hydrogen atoms. These were substituted in the equations for the polarization of the carbon atoms, and their solution gave a better approximation to the true values. The operation was repeated a few times until further approximations did not cause any appreciable alteration in the values.

When the field is parallel to the X-axis, the following values were obtained for the polarizations parallel to the field.

$$ex_1 = 1 \cdot 53 \text{ Ex } 10^{-24}$$
$$ex_2 = 1 \cdot 98 \text{ Ex } 10^{-24}$$
$$ex_1' = 0 \cdot 64 \text{ Ex } 10^{-24}$$
$$ex_2' = 0 \cdot 11 \text{ Ex } 10^{-24}$$

where ex_1', ex_2' refer to the hydrogen atoms. The resultant polarization parallel to the X-axis is $4 (ex_1 + ex_1') + 2 (ex_2 + ex_2')$, i.e., $12 \cdot 86 \text{ E} \times 10^{-24}$.

With the field parallel to the Z-axis, the polarizations of the carbon and hydrogen atoms parallel to the field were

$$ez_1 = 0 \cdot 52 \text{ E} \times 10^{-24}$$
$$ez_1' = 0 \cdot 29_5 \text{ E} \times 10^{-24}$$

and thus we get for the resultant polarization $6 (ez_1 + ez')$ the value $4 \cdot 88$ $\text{E} \times 10^{-24}$.

The polarization when the field is parallel to the Y-axis would be the same as when it is parallel to the X-axis.

The calculated value of the depolarization of the transversely scattered light is $0 \cdot 074$, which may be compared with the experimental value $0 \cdot 067$.

4. The Molecular Refractivity of Benzene.

The mean polarization per unit field averaged over all orientations is $(A + B + C)/3$. With the values obtained in the last section, its value is $10 \cdot 2 \times 10^{-24}$. Calculating the molecular refractivity by means of the formula

$$\frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_0 \frac{A + B + C}{3},$$

we find its value to be $25 \cdot 9$ (for the F line). The experimental value of the

molecular refractivity of benzene* is $26 \cdot 2$ for the D line and $26 \cdot 7$ for the F line. The difference is not large considering the nature of the assumptions involved in the calculations. It may be recalled that the atomic refractivities of carbon and hydrogen which we have used are not the refractivities deduced from the molecular refractivities of organic compounds by the rule of additivity. Such values are likely to be invariably higher owing to the influence of the other atoms in the molecule. If we adopt a plane structure, both the refractivity and the anisotropy are found to be too high.

5. *Optical Anisotropy and Refractivity of Cyclohexane* (C_6H_{12}).

Compared with benzene, cyclohexane has a small anisotropy; while the depolarization of the transversely scattered light in the former is $0 \cdot 067$, that in the latter is only $0 \cdot 011$. The extra hydrogen atoms should therefore occupy such positions as will reduce the anisotropy. If we retain the idea that the binding of one carbon atom to another and of a hydrogen to a carbon take place at the tetrahedral angle, the structure of cyclohexane can be derived from that of benzene by adding a hydrogen to each carbon atom, the extra hydrogens being alternately below and above the plane of the paper in fig. 2. The new hydrogens attached to carbon atoms 1, 3 and 5 will be vertically below the plane of the paper, while those attached to 2, 4 and 6 will be vertically above the plane. We assume that the distance of the optical centres of these hydrogen atoms from the centres of the neighbouring carbon atoms to be the same as before, namely $1 \cdot 43$ A.U. We can now calculate the optical anisotropy of such a structure. When the field is parallel to the X- or Y-axis, the polarization of the extra hydrogens (which we shall denote by ex_1'', ex_2'', etc.) will cause a field at the carbons tending to reduce their polarization, and the polarization of the carbons will similarly tend to reduce the field at the hydrogens while when the field is parallel to the Z-axis, the polarizations will help each other. Using the same method of successive approximations, and neglecting the mutual influence of the previous set of hydrogen atoms on the new set, the following values are obtained for the polarisations parallel to the field :

$$ex_1 = 1 \cdot 47 \ \ E \times 10^{-24}$$
$$ex_2 = 1 \cdot 90 \ \ E \times 10^{-24}$$
$$ex_1' = 0 \cdot 63 \ \ E \times 10^{-24}$$
$$ex_2' = 0 \cdot 12 \ \ E \times 10^{-24}$$
$$ex_1'' = 0 \cdot 15 \ \ E \times 10^{-24}$$
$$ex_2'' = 0 \cdot 09 \ \ E \times 10^{-24}$$

* 'Landolt Bornstein Tabellen,' p. 977.

K 2

Therefore, total polarization parallel to the X-axis $= 13 \cdot 2$ E $\times 10^{-24}$, and

$$ez_1 \;\; = 0 \cdot 86 \text{ E} \times 10^{-24}$$
$$ez_1{}' = 0 \cdot 21 \text{ E} \times 10^{-24}$$
$$ez_1{}'' = 0 \cdot 63 \text{ E} \times 10^{-24}$$

Therefore, total polarization parallel to the Z-axis $= 10 \cdot 2$ E $\times 10^{-24}$.

From the similarity to the case of benzene, the polarization parallel to the Y-axis will be the same as that parallel to the X-axis, and hence the value of the anisotropy is $13 \cdot 2 : 13 \cdot 2 : 10 \cdot 2$. The calculated value of r is $0 \cdot 008$.

The average polarization obtained from the above data is $12 \cdot 2$ E $\times 10^{-24}$ and the calculated molecular refractivity $31 \cdot 0$, while the observed refractivity is $29 \cdot 7$ for the D line and $30 \cdot 1$ for the F line. The difference is not large considering the somewhat arbitrary way in which we fixed the atomic refractivities.

One noteworthy feature of the optical anisotropies of individual molecules is the high values of their double refraction compared with those of crystals. For example, potassium nitrate, which is a strongly doubly-refracting crystal, has for the ratio of its principal refractive indices the value $1 \cdot 587 : 1 \cdot 336$, i.e., $1 \cdot 19 : 1$, while a benzene molecule, which is also an example of a molecule with fairly high anisotropy, has for its corresponding ratio the value $2 \cdot 45 : 1$. The enormous decrease in the value of the anisotropy when the molecules get arranged into a crystal is due to the influence of the polarization of the atoms in the neighbouring molecules, which, being arranged on all sides of the molecule under consideration, tend to make its polarization more isotropic. A similar instance is furnished by the change in passing from benzene to cyclohexane.

6. *Summary.*

Developing the idea put forward in Part I that the optical anisotropy of gaseous molecules which is responsible for the partial depolarization of the light scattered in a direction perpendicular to the incident beam, can be explained to a large extent by the mutual influence of the electrical doublets induced in the different atoms of the molecule by the electric field of the incident radiation, the optical anisotropy of benzene has been calculated for two different structures. Each atom is assumed to be isotropic. If the six carbon atoms are assumed to lie in a plane with their centres at the corners of a regular hexagon, as in graphite, the optical anisotropy comes out too high even when the hydrogens are ignored. If, on the other hand, the carbon atoms are arranged in a puckered ring, as in diamond, and the hydrogens are joined to the carbons

at the tetrahedral angle, the calculated and observed values of the optical anisotropy agree well, when the atomic refractivity of carbon is assumed to be that of diamond and the atomic refractivity of hydrogen to be that in gaseous hydrogen. The calculated and observed values of the molecular refractivity also show good agreement.

The calculation is extended to cyc ohexane. The six extra hydrogen atoms are supposed to be attached to the carbon atoms alternately on each side of the approximate plane of the carbon ring. The calculation shows that a considerable falling off in anisotropy is to be expected, which is borne out by experiment. The calculated refractivity is also in fair agreement with the experimental value.

A simple glass apparatus is described for the measurement of the imperfection of polarization of the light scattered by vapours which require heating for their production.

I am very thankful to Prof. C. V. Raman for his kind and encouraging interest in the work.