

The Magnetic and Optical Properties of the Benzene Ring in Aromatic Compounds

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deduction* of the experimental fact that the K electrons have an average forward momentum which is greater than the momentum $h\nu/c$ of the incident quantum. Consequently, attempts at a theoretical interpretation of the above results will await the appearance of his paper.

The Magnetic and Optical Properties of the Benzene Ring in Aromatic Compounds.

By S. BHAGAVANTAM.

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1. *Introduction.*

The present paper describes the third of a series of investigations undertaken at the suggestion of Sir C. V. Raman of the remarkable magnetic and optical characters exhibited by organic crystals of the aromatic class. In the earlier papers the author had described the optical and the magnetic characters of naphthalene crystals† and also of anthracene and other organic compounds‡ and discussed the significance of the results. In all these cases, however, the fact that there were two or more molecules per unit cell in the crystal lattice, and that the X-ray results available did not fix with sufficient precision either the form of the molecules or their orientation relatively to each other and to the crystal lattice prevented a complete interpretation of the results. Mrs. Lonsdale's recent admirable investigation of the structure of hexamethylbenzene§ has made further and very significant progress possible. She has shown that this substance crystallises in the triclinic system with one molecule per unit cell and that the carbon atoms in the molecule form flat hexagonal rings parallel to a cleavage plane. Hence this substance forms a very suitable material for the experimental study of the magnetic and optical characters of the benzene ring in its substitution products. It has accordingly been used as the starting point in the present investigation.

* Sommerfeld, "Atombau und Spektrallinien," Wellenmechanischer Ergänzungsband, (1929).

† 'Roy. Soc. Proc.,' A, vol. 124, p. 545 (1929).

‡ 'Ind. Jour. Phys.,' vol. 4, p. 1 (1929).

§ 'Roy. Soc. Proc.,' A, vol. 123, p. 494 (1929).

2. *Crystal Form and Structure of $C_6(CH_3)_6$.*

For convenience of reference Mrs. Lonsdale's results will be briefly recalled here. The nomenclature adopted is the same as hers. The substance crystallises out of benzene mostly in parallel plates with the bc plane prominently developed. Often there are two other pairs of faces, fairly well developed, which were chosen by her as the ab and ac planes. The unit cell thus defined is a triclinic cell which was found to have the following axes and axial angles :—

A.U.		°	'
9·010	44	27
8·926	116	43
5·344	119	34

The crystal is centrosymmetrical with one molecule per cell.

The faces have been identified by measuring under a microscope, the angles between the bounding lines on each face. Fig. 1 shows the shape of the crystal

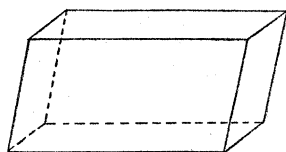


FIG. 1.

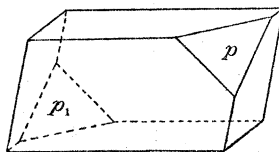


FIG. 2.

usually obtained and described by Mrs. Lonsdale. Very often the crystal takes the form shown in fig. 2 with the acute angled corners truncated by another pair of faces p and p_1 in addition to the three pairs already noted by Mrs. Lonsdale. From a measurement of the angles on the bc and the ab faces, the indices of these two new faces have been deduced as 221. A reference to fig. 4, which represents the structure of the ab plane, will make it clear why the 221 faces occur only at the acute-angled corners, for the presence of such a face at the obtuse angled corner interferes with the integrity of the molecules. On making up a model it will be further seen that these faces do not cut any other molecules, but pass through the centres of those that lie at the corner of an adjacent cell. This involves a comparatively less reticular density in the plane and explains its less frequent occurrence.

The unit cell and the structure of the ab plane are represented diagrammatically in figs. 3 and 4 respectively. The crystal consists of flat molecule layers piled one over the other parallel to the ab plane, the successive layers being displaced relatively to each other. As a result of this displacement, the c

axis is not normal to this face but makes $44^{\circ} 27'$ and $116^{\circ} 43'$ with the b and the a axes respectively. The carbon atoms constituting each molecule have

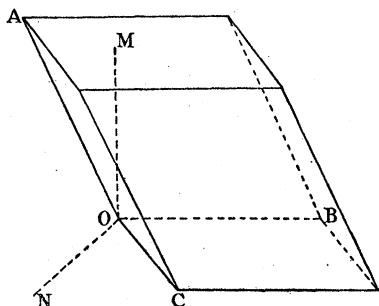


FIG. 3.

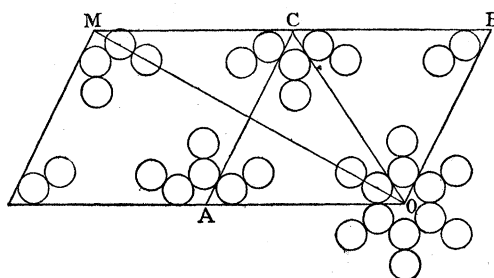


FIG. 4.

been placed by Mrs. Lonsdale in the ab plane in such positions that the a and the b axes do not stand symmetrically with respect to the benzene ring. She has considered the effect of rotating the ring in its own plane on the calculated structure factors and showed that the agreement was most satisfactory when the direction symmetrical with respect to the benzene ring makes an angle which is a little over 6° with the b axis (OB in fig. 4). Nevertheless OB stands out as a crystallographic axis.

3. Magnetocrystalline Properties.

When the crystal is suspended free to rotate in a uniform magnetic field with the ab face horizontal, the b axis sets itself along the field. When this face is vertical, the b axis remaining horizontal, it turns round again with a comparatively stronger moment and sets with that axis along the field. If the crystal is suspended with the b axis vertical, the ab face falls into parallelism with the field. From these observations it is clear that OB in fig. 3 is one of the principal magnetic axes along which the magnetic susceptibility is a minimum and a line perpendicular to the ab face is another principal axis along which the susceptibility is a maximum. The direction of the intermediate value is consequently perpendicular to both these. These are shown in fig. 3 by the three lines OB, ON and OM respectively. When the ab face is horizontal, the crystal turns round in a uniform field and sets with the b axis parallel to the field, although very often the crystals are prisms elongated along this axis. Nevertheless the couple is relatively weak, but it is significant in that it implies a magnetic asymmetry in the plane of the ring.

An ordinary Curie balance is employed in determining the principal susceptibilities. Three observations are made with a weighed crystal, each

principal axis being brought in turn into parallelism with the field. The balance is standardised with a small diamond of known weight and susceptibility which belongs to the cubic system. The mean values obtained from observations on two crystals are set forth in Table I, the necessary correction for the glass fibre and the Canada balsam used in sticking the crystal having been made.

Table I.

Direction as in fig. 3.	Ratio.	Gram-molecular susceptibility.
OB	1.0	-105×10^{-6}
OM	1.1	-116×10^{-6}
ON	1.8	-190×10^{-6}

The mean of the three principal susceptibilities works out to be -137×10^{-6} whereas the susceptibility calculated from Pascal's additive constants comes out as -127×10^{-6} . The order of the susceptibilities is in accordance with the indications afforded by the behaviour of the crystal in a uniform field. The diamagnetic susceptibility along a direction perpendicular to the plane of the benzene ring is the largest. This happens to be so in spite of the fact that the crystallographic axis is inclined considerably away from the normal. In other words, the crystalline properties seem to be largely determined by those of the molecule itself. It was remarked that there is a small asymmetry in the plane which manifests itself as a weak turning moment in a uniform field. From the above quantitative data this is seen to be of the order of 10 per cent. This significant fact will be recalled at a latter stage.

4. *Optical Properties of the Crystal.*

All the observations have been made under a polarising microscope with monochromatic illumination. The directions of extinction on the *bc* face have been carefully examined with a view to find out the deviation, if any, from the *b* axis analogous to the structural deviation of symmetry referred to before, but none was detectable. The extinction is found to remain perfectly parallel to the *b* axis. On the 001 face they are again parallel to the *b* axis and a line perpendicular to it. Thus *b* is one of the principal axes of the optical ellipsoid and the other two consequently lie in a plane perpendicular to the same. When the light passes normal to the 100 face, the crystal shows an interference figure in convergent light between crossed nicols consisting of several rings even for very small thicknesses, indicating a high

degree of anisotropy. Neither of the optic axes is visible in the field, but the obtuse bisectrix can be seen to emerge at a certain inclination to the normal. The axial plane is perpendicular to the b axis. This means that the b axis is one of the principal axes, in agreement with the above observations and the crystal has an intermediate refractive index for incident light vibrating along this axis. It is mentioned before that the crystal has a very good cleavage parallel to the ab face and this fact is taken advantage of in viewing the axial figure for incidence normal to this face. A well-developed crystal is cleaved and a thin plate parallel to the 001 face is thereby obtained. The interference figure through the same shows the acute bisectrix, quite in the centre of the field.

In the notation of fig. 3 the principal axes of the optical ellipsoid will therefore be represented by OB, OM and ON as OB is the b axis and ON is perpendicular to the ab face. These principal directions undergo no detectable change with the wave-length, which may be attributed to the simplicity of crystal structure. The quantitative data to be given later show that along ON the refractive index is a minimum. This direction of least optical polarisability is normal to the plane of the benzene ring and is apparently not influenced by the structural displacement of the successive layers. Thus the crystalline optical properties are again largely determined by the molecule itself. The restoration of light between crossed nicols when it passes normal to the 001 face is quite distinct, which implies an optical asymmetry in that plane analogous to the magnetic asymmetry. This will be discussed more fully later.

The fact that the crystal has at least three pairs of plane parallel surfaces developed on it is taken advantage of in making use of an interferometric method. Light from a brilliant point source is rendered parallel by means of a lens and is polarised by a nicol. The polarised parallel beam passes through another nicol and falls on the slit of a wave-length spectrometer. When the nicols are not crossed, a continuous spectrum extending over the entire visible region is seen in the field of vision. When the nicols are crossed and an anisotropic plate introduced between them in a favourable position, there is restoration of light and the slit is once again illuminated. The two compounds into which the polarised beam is split up by the passage through the crystal are in a position to interfere if the crystal plate is really plane parallel and the entire field is covered with alternating bright and dark bands. The wave-length λ corresponding to the position of the n th dark band is connected with the thickness of the crystal plate by the equation $n\lambda = t(\mu_1 - \mu_2)$, where $\mu_1 - \mu_2$ is the retardation produced by the crystal plate, if it were of

unit thickness, between the two components. The number of bands visible in the field depends upon the thickness and the birefringence of the plate. If the thickness, the order of the interference band and the wave-length corresponding to its position are known, then the difference between the principal indices in the plane normal to which the light is incident can be calculated. It is essential that light should enter and emerge in a direction which is normal to the crystal plate. Otherwise the results are considerably complicated by refraction within the crystal plate. The order of any particular band can be arrived at by a consideration of the wave-lengths corresponding to two consecutive bands, by assuming that the difference between the principal indices in the plane does not change appreciably if the wave-lengths are close enough.

Such observations are made with two pairs of faces (100 and 001) interposed perpendicular to the beam of light. In the former case, the number of bands visible is very large, indicating a large birefringence, whereas in the latter, even for fairly thick sections, the number of bands visible in the field is much smaller, indicating a considerably weaker birefringence. Owing to the greater thickness the general intensity is also very much feebler, that it necessitates the concentration of the light on to the slit of the spectrometer by means of an additional lens. Further, after the light is adjusted to normal incidence at the 100 faces, the crystal is slightly rotated about the b axis and as a consequence the entire band system moves to one side up to a certain point, after which further rotation of the crystal causes it to retrace back. At this point the birefringence is a maximum, *i.e.*, light inside the crystal is passing along one of the axes of the optical ellipsoid and the interfering components differ by a retardation corresponding to $b - c$ where b is the intermediate and c the minimum refractive indices. At this stage light passes in the crystal plate at an inclination of about 10° to the normal to the face and hence the effective thickness of the crystal is slightly increased. Introducing this correction, the phase differences are again calculated at the several wave-lengths corresponding to the interference bands. Thus three equations involving a , b and c are furnished and generally suffice for their solution. An additional observation is made by immersing the crystal in cedar oil, whose refractive index and dispersion are previously determined by an Abbe Refractometer. The values calculated for certain wave-lengths from these data are given below in Table II.

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Table II.

Wave-length. A.U.	$a - b.$	$b - c.$	$a - c.$	$a.$	$b.$	$c.$
6230	0·0542	0·2443	0·2985	1·7987	1·7445	1·5002
5870	0·0537	0·2443	0·2980	1·8012	1·7475	1·5032
5560	0·0533	0·2451	0·2982	1·8042	1·7509	1·5058
5310	0·0531	0·2460	0·2991	1·8069	1·7538	1·5078
5090	0·0531	0·2473	0·3004	1·8098	1·7567	1·5094

a , b and c represent the refractive indices of the crystal for the incident vibrations taking place along OM, OB and ON respectively (fig. 3). The data clearly show that the dispersion is very weak, unlike the cases that are usually met with in the organic field.

5. *Relation between the Magnetic and Optical Characters.*

Table III.

Direction as in fig. 3.	Gram-molecular susceptibility.	Refractive index.
ON	-190×10^{-6}	1·5032
OM	-116×10^{-6}	1·8012
OB	-105×10^{-6}	1·7475

In Table III the magnetic susceptibilities and the refractive indices for a particular wave-length are given together. The directions of the largest diamagnetic susceptibility and the least optical polarisability coincide, a phenomenon which is typical of the aromatic class of substances. In the plane of the benzene ring, along the line OM, the magnetic susceptibility is intermediate, whereas the optical polarisability is greatest and along OB the former takes the least value and the latter takes an intermediate value. In other words in the ring itself, the sequence of magnitude is the same for both the magnetic and optical moments, a case which very often occurs in the aliphatic class of compounds but never observed so far in any of the aromatics. The methyl groups, the substitution of which takes place symmetrically at all the corners of the hexagon, alter the magnitudes of the principal optical and the magnetic moments in the molecule to a certain extent, although the directions of the largest magnetic susceptibility and the least optical polarisability still remain normal to the plane of the ring. They introduce the above curious reversal in the plane of the ring contrary to the usual phenomenon

observed in aromatics. That this is purely an effect of the methyl groups is clear from the data regarding a pure aromatic substance, for *e.g.* naphthalene,* which show nothing of the kind.

6. Relation of Birefringence to Optical Anisotropy of the Molecule.

As stated above, the birefringence of the crystal clearly arises from the optical anisotropy of the individual molecule and can be quantitatively connected with it, provided the influence of the surrounding molecules can be evaluated. This may be accomplished by taking the field acting on the molecule to be that at the centre of a cavity scooped out of the entire medium and having the geometrical form of the molecule itself. In the present case, this cavity may be taken to have the form of an oblate spheroid of revolution with the principal axes equal to 9.0 and 3.69 A.U. respectively. The field at the centre of such a spheroidal cavity may be expressed in terms of the constants p_1 , p_2 , p_3 given by the relations

$$p_1 = p_2 = 2\pi \left(\frac{\sqrt{1-e^2}}{e^3} \sin^{-1} e - \frac{1-e^2}{e^2} \right)$$

$$p_3 = 4\pi \left(\frac{1}{e^2} - \frac{\sqrt{1-e^2}}{e^3} \sin^{-1} e \right),$$

where e is the eccentricity of the spheroid. A, B and C, the moments induced in an individual molecule, are connected with A', B' and C', the moments actually observed in the crystalline state, by the equations

$$A' = A (1 + p_1 \chi_1),$$

$$B' = B (1 + p_2 \chi_2),$$

$$C' = C (1 + p_3 \chi_3).$$

χ_1 , χ_2 and χ_3 represent the susceptibilities of the medium ($\mu_1^2 - 1/4\pi$), etc., respectively in the three directions. From the equations A, B and C can be easily calculated. The optical anisotropy of the molecule is conveniently defined by a magnitude r which is connected with A, B and C by the relation

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

The value of r for any given molecule can be ascertained directly by observations on the depolarisation of light scattering in the state of vapour. In Table IV, the values of r for vapours of benzene, toluene and *m*-xylene† are

* *Loc. cit.*

† Data are from I. R. Rao, 'Ind. J. Phys.', vol. 2, p. 61 (1927).

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given together with the value for hexamethylbenzene calculated in the manner explained above from the birefringence of the crystal. It will be seen that there is a slow progressive increase in the optical anisotropy of the molecule with increasing number of methyl groups in it.

Table IV.

Substance.	Benzene.	Toluene.	<i>m</i> -Xylene.	Hexamethylbenzene.
<i>r</i>	0·042	0·046	0·046	0·048

7. *Effect of the Methyl Groups on the Anisotropy of the Benzene Ring.*

On the Langevin theory of diamagnetism, the diamagnetic susceptibility of atoms arises from the Larmor precession of the electronic orbits in a magnetic field. The theory pre-supposes a freedom for the orbits to precess. That these considerations are not wholly applicable to polyatomic molecules, in which the large electronic orbits have fixed orientations in the molecule, was pointed out by Raman and Krishnan.* They assumed that all the electronic orbits in the benzene molecule corresponding to the C — C bonds lie in the plane of the ring, and those corresponding to the C — H bonds in planes perpendicular to it, and computed its magnetic anisotropy on the basis that each orbit gives rise to a diamagnetic susceptibility along a direction normal to its own plane. The orbits were assigned values deduced from Pascal's additive data in the field of aliphatic compounds. The computation gave results agreeing with those deduced from the observed magnetic birefringence in liquid benzene, and hence we may extend the ideas on which it was based to the case of some benzene derivatives. The cases of toluene, para- and meta-xylenes and hexamethylbenzene have been considered, taking all the substituted methyl groups into consideration. The electronic orbits connecting the nuclear carbon atoms to each other are again assumed to be in the plane of the benzene ring and those connecting them to the carbons of the methyl groups normal thereto. Further, a tetrahedral distribution of the hydrogen atoms is assumed, with the C — H orbits so oriented that their contribution is equally divided in and perpendicular to the plane of the benzene ring. This can be accomplished by rotating each orbit around the major axis till the

* Raman and Krishnan, 'Compt. Rend.,' vol. 184, p. 449 (1927). Compare also M. G. Foex, 'Compt. Rend.,' vol. 188, p. 1154 (1929).

normal to it makes an angle $\cos^{-1}(1/\sqrt{3})$ with the direction of the corresponding aliphatic C — C bond. The bonds are assigned values deduced from Pascal's additive data in the field of aliphatic compounds. Under such conditions the calculated and observed values agree very closely and the plane of the ring is rendered slightly asymmetric in all cases except hexamethylbenzene. For this substance, however, the result is not in complete agreement with experience, since, as already remarked, we actually have a feeble asymmetry to the extent of 10 per cent. in the plane of the ring. This point will be dealt with in greater detail in the next section. Table V shows the ratio of the susceptibility normal to the plane of the ring to the susceptibility averaged over all directions parallel to the plane of the ring.

Table V.

Substance.	Benzene.	Toluene.	<i>p</i> -Xylene.	<i>m</i> -Xylene.	Hexamethylbenzene.
Calculated	2.1†	1.94	1.80	1.80	1.6
Observed	2.1*	1.94*	1.80*	1.80*	1.7‡

* Computed from data on magnetic birefringence.

† From Raman and Krishnan, *loc. cit.*

‡ From Table I.

As will be seen from the table, the agreement is perfect in toluene and xylenes and is satisfactory for hexamethylbenzene. It will be further seen clearly from Tables IV and V that *the influence of the methyl groups is to diminish the magnetic anisotropy and to enhance the optical anisotropy of the benzene ring.*

8. *Asymmetry in the Plane of the Ring.*

It will be noticed from the data given in section 2 that there is a pseudo-hexagonal symmetry in the *ab* plane, the angle differing from 120° only by $26'$ and the axes differing from each other by only about 1 per cent. The asymmetry in this plane is ascribed by Mrs. Lonsdale to a probable lack of symmetry in the benzene ring itself together with a variation in the orientation of the attached methyl groups. The crystallographic asymmetry bears a close analogy to the optical and the magnetic asymmetries mentioned before. In this plane the principal magnetic susceptibilities and the refractive indices differ by about 10 per cent. and 3 per cent. respectively.

Every molecule in the *ab* plane is surrounded by six other nearest neighbours situated at the corners of a hexagon very nearly regular and hence an attempt to ascribe the optical anisotropy in that plane to the mutual action of the induced doublets proves unsuccessful. Further, any attempt to explain the observed magnetic anisotropy in terms of the mutual influence between the local fields will also prove a failure. All these considerations lead us to the same conclusion as before that the properties of the crystal are to a large extent determined by those of the molecule and we are forced to ascribe the observed birefringence in the *ab* plane to an intrinsic asymmetry in the molecule itself. With the accepted notions of the structure of the benzene nucleus, and the chemical equivalence of the six carbon atoms, it is hard to understand why the ring exhibits such a lack of symmetry although very small, but persisting crystallographically, optically, and magnetically.

In the previous section, it is assumed that the three (C — H) electron orbits of each methyl group are all identical, which led to an isotropy in the plane of the benzene ring for hexamethylbenzene contrary to the observed facts. Such an assumption is not justified, especially in view of the crystallographic evidence recently pointed out by Mrs. Lonsdale.* She proposed centrosymmetrical structures for benzene and naphthalene† molecules on the basis of an anisotropic carbon atom in which the four outer valency electrons are all not similar but fall into two pairs whose valencies differ slightly in a geometrical sense. This has a further support from spectroscopic observations, namely, that two of the outermost electrons in carbon move in 2_1 orbits while the other two move in 2_2 orbits, a conclusion which has been definitely established by Millikan and Bowen‡ recently. Once this difference is accepted, it will at once be seen that the methyl group can no longer contribute to the magnetic susceptibility equally in all the directions, and it is easy to understand why the ring is anisotropic in its own plane.

Thus the 18 (C — H) electron orbits present in hexamethylbenzene fall into two different groups, all the members of each group being similar in themselves. The ratio of the contributions of these two different groups necessary to produce the observed diamagnetic anisotropy in the plane of the ring can be easily calculated. Taking the observed anisotropy, *i.e.*, 10 per cent. to be truly representative of the molecule, this ratio comes out as 15 : 29. This suggests

* 'Phil. Mag.,' vol. 6, s. 7, p. 433 (1928).

† 'Proc. Leeds Phil. Soc.,' vol. 1, p. 346 (1928).

‡ 'Phys. Rev.,' vol. 26, p. 310 (1925).

that the areas of the corresponding electron orbits differ by the same order of magnitude.

9. *Summary and Conclusion.*

The magnetic and optical characters of hexamethylbenzene crystals have been studied and their theoretical significance is discussed.

The principal gram-molecular magnetic susceptibilities are -190×10^{-6} , -116×10^{-6} and -105×10^{-6} . The principal refractive indices for 5870 A.U. are 1.8012, 1.7475 and 1.5032. The dispersion is weak.

The directions of maximum magnetic susceptibility and the minimum optical polarisability coincide with each other and also with the normal to the plane of the benzene ring. Both of these phenomena are believed to be characteristic of the aromatic class of compounds. In the plane of the ring there is a slight magnetic and optical anisotropy, the directions of the greatest optical and the magnetic polarisabilities coinciding: the latter feature has been previously observed in several aliphatic compounds, and hexamethylbenzene appears therefore to simulate an aliphatic compound in its behaviour so far as the plane of the benzene ring is concerned.

The observations indicate that the magnetic and optical characters of the crystal are practically determined by the magnetic and optical anisotropy of the molecule itself and indeed the observations with the crystal fit very well with the values for the molecular anisotropy for benzene derivatives in the fluid state derived from studies on light-scattering and magnetic birefringence. The addition of methyl groups is found to diminish the magnetic and enhance the optical anisotropy of the benzene ring.

The theoretical computations made by Raman and Krishnan of the magnetic anisotropy of the benzene molecule have been extended to the cases of its methyl derivatives, and the results obtained are in satisfactory agreement with observation. An explanation for the asymmetry in the plane of the ring is offered on the basis of an anisotropic carbon atom, the orbital areas of whose valency electrons are all not identical.

I have much pleasure in expressing my heartfelt thanks to Sir C. V. Raman, F.R.S., under whose kind guidance the work was carried out. Special acknowledgments are also due to Prof. C. K. Ingold, F.R.S., of Leeds University, whose great kindness in furnishing some very pure hexamethylbenzene made the research possible. The investigation was conducted in the laboratory of the Indian Association for the Cultivation of Science, Calcutta.
