The relation between colour and molecular structure in organic compounds

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Abstract

(a) After a brief review of the existing theories, the paper considers the relationship between colour and constitution in organic compounds from a new and fundamental standpoint suggested by a comparison of the *structure and the physical properties of diamond and graphite.*

(b) *A remarkable and very general parallelism* between the *colour or light absorption,* and the degree of optical, electrical, and magnetic *anisotropy of the molecules* is revealed on an examination of the data of (a) light absorption, (b) light scattering, (c) electric birefringence, (d) magnetic birefringence, (e) magnecrystalline behaviour, and (f) crystalline birefringence of carbon compounds. Those structures and groups that tend to favour the development of colour also tend in general to enhance the degree of optical, electrical and magnetic anisotropy of the molecule. The facts covered by the "theory of chromophores and auxochromes", the "quinonoid hypothesis" and "the strain theory of colour" are simultaneously included within this single generalisation.

(c) *A theoretical basis for the generalisation* is furnished by the electron theory of dispersion, taken together with certain hypotheses (due to J J Thomson and L Silberstein) regarding the origin of the optical anisotropy of molecules, which are supported by observational data regarding refractivity, dispersion and pleochroism of organic compounds.

(d) *The mechanism of light-absorption* is briefly discussed, with reference to electrical conductivity, and the special type of photoconductivity observed in illuminated crystals of high refractive index.

1. Introduction

The older theories of colour in organic chemistry such as the theory of chromophores and auxochromes and the quinonoid hypothesis are adequately

discussed in well-known treatises to which the reader may be referred.[1] These theories are essentially chemical in their outlook, and their utility lay in their power to guide the labours of the synthetic colour chemists. They do not however, pretend to offer any physical explanation of the relationships between structure and light absorption. Some recent theories, especially those proposed by Stieglitz[2] and by Sikhibhushan Dutt[3] are more distinctly physico-chemical in character and may be briefly noticed. According to Stieglitz, colour production is essentially due to the simultaneous presence of oxidising and reducing groups in the chemical molecule. He regards the chromophoric and the auxochromic groups of the old structural theory as the oxidising and the reducing halves of the dye molecule. The vibrations of the electrons in the reducing group are so affected by the proximity of the oxidising group that the absorption frequencies are considerably decreased. The proper choice and substitution of the said groups in the nucleus intensifies this effect and the molecule begins to absorb portions of the visible spectrum; and thus develops colour. In the process of absorption, according to Stieglitz, there is no actual transfer of electrons between the different groups but they are still held within atomic restraints.

Sikhibhushan Dutt's theory is on quite different lines. According to him, selective absorption is due to molecular strain produced by any one of the following causes; (a) formation of a double or a triple bond, (b) formation of a cyclic from an open chain compound and (c) unequal distribution of the masses attached to the atom. He studied the internal strain of a number of double bonded systems and arranged them in the increasing order of magnitude as C:C, C:O, C:N, N:N, N:O. A strain-free molecule is regarded by him as an elastic and almost frictionless system which transmits all radiations. He assumes that by the introduction of a double bond, a frictional force is brought into play, and that the molecule begins to resonate with vibrations of lower frequency and hence absorbs in the ultraviolet region. With increasing strain, the frequency decreases and the substance develops absorption in the visible region.

In the present communication, the whole subject is approached from a different and more fundamental standpoint. The element carbon as is well known, can assume two crystalline forms which differ in their properties in a most remarkable way. The first form, diamond is a transparent and colourless crystal. The second is graphite which is black and quite opaque. In this fundamental fact regarding carbon itself, it would seem that we can find the clue to a general explanation of

[1]Cohen, Treatise on Organic Chemistry, Vol. II.
Colour in Relation to Chemical Constitution by E R Watson, Longmans (1918).
Physikalische Eigenschaften and Chemischen Knonstitution, W Kanffmann (Enke, 191).
[2]Julius Stieglitz, A theory of colour production, Franklin Institute, Centenary Lecture, 1924.
[3]Sikhibhushan Dutt, A theory of colour on the basis of molecular strain, J C S, Vol. 1928, p. 1171, 1926 and J. Indian Chem. Soc. 4, pp. 99 and 265.

the immense variety of facts known concerning the colour of carbon compounds. Why is graphite black while diamond is transparent though chemically they are both carbon? The answer to this question is presumably to be found in the structure of diamond and graphite respectively. In the diamond, as is shown by X-ray analysis, each atom of carbon is united in a very similar way to four others and the whole structure is symmetrical and the crystal belongs to the isotropic system.

In graphite, on the other hand, the atoms lie in plane hexagonal networks in such manner that each atom is placed close to three others lying in the same plane with it, and much further away from a fourth atom lying in an adjacent hexagonal net plane. As a consequence, the whole structure of graphite is *intensely anisotropic*. This is shown in the clearest way by its diamagnetic behaviour. According to Owen,[4] also Honda and Sone,[5] the crystal is magnetisable about 6 times more in a direction perpendicular to the hexagonal plane, than in directions parallel to the plane. The fact that graphite is a conductor of electricity, and therefore according to known principles opaque to light, must stand in the closest relationship to the ascertained structure of the substance. According to Washburn,[6] the electrical conductivity in the hexagonal plane is about a hundred times as large as in directions parallel to the principal axis. Single crystals, in the form of thin transparent flakes, have also been examined optically, and were found to be negatively birefringent with a strong pleochroism accompanied by a large anisotropic effect.[7]

When we pass to consider the vast field of organic compounds exhibiting colour, we find that in most artificial and natural dyestuffs, the carbon atoms form closed rings of which there may be several condensed together in a molecule, somewhat similar to the plane hexagonal networks of carbon atoms in graphite. Investigations which will be referred to in the following pages show that the structures in organic compounds which according to Sikhibhushan Dutt produce "molecular strain" are highly anisotropic in their optical, electrical and magnetic properties in a manner analogous to the behaviour of graphite. It is not surprising, therefore, that at the same time they also tend like graphite to absorb light and thus to exhibit colour. The intensity and nature of the colour depend on the portion of the spectrum absorbed. Here, the finer details of the molecular structure play an important part. We shall set out in this paper the evidence which connects anisotropy and colour in carbon compounds and indicates a common origin for both of these optical characters.

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[4]M Owen, *Ann. Physik* 1912, **37**, 657.
[5]Kotaro Honda and Take Sone, *Sci. Rep. Tohoku Imp. Univ.* Series I, (1913) **2**, 25.
[6]G E Washburn, *Ann. Phys.* (1915). **48**, 236.
[7]P Gaubert, *Comptes Rendus* (1923) **171**, 1123.
See also Paul Ramdhor, *Chem. Abst.* (1929) **23**, 1738.

2. Absorption spectra of organic compounds

Much work has been done on the relation between molecular absorption and the chemical constitution in the organic field and a detailed discussion of the subject is given in many treatises, especially those of Kauffmann and Watson already referred to. Here, data for a few organic compounds are collected together, in order to illustrate some important points.

Table I. Structure and absorption

Series	Substance	Structure	Absorption			
			λ_1	λ_2	λ_3	λ_4
(1)	Benzene		2610	2540	2490	2440
	Naphthalene		2850	2720	2630	2550
	Anthracene		—	3600	3430	3280
	Naphthacene		Orange			
(2)	Azomethane	$CH_3—N{=}N—CH_3$	3480			
	Methaneazobenzene	$CH_3—N{=}N—C_6H_6$	4070			
	Azobenzene	$C_6H_5—N{=}N—C_6H_5$	4530			
(3)	Benzophenone	$C_6H_5—CO—C_6H_5$	White			
	Benzil	$C_6H_5—CO—CO—C_6H_5$	Bright yellow			
	Diphenyl triketone	$C_6H_5—CO—CO—CO—C_6H_5$	Golden yellow			
	Diphenyl tetraketone	$C_6H_5—CO—CO—CO—$ $CO—C_6H_5$	Red			

The table clearly shows several striking features. A passage from benzene via naphthalene and anthracene to naphthacene, which contain increasing numbers of benzene nuclei is accompanied by a marked shift in the absorption bands from the far ultraviolet towards the red end of the visible spectrum, until finally in naphthacene, portions of the visible spectrum are absorbed, the substance developing colour. The development of colour may be taken to mean in a wider sense, a development of smaller absorption frequencies, the absorption bands thereby shifting nearer the visible region. The same tendency is to be seen in the next series. The aromatic groups are clearly more conducive to the development of colour as the transition from azomethane via methaneazobenzene to azobenzene

shows. The next series shows the influence of a carbonyl group (C:O). Starting with benzophenone, which is colourless, containing one C:O group, the colour can be deepened by increasing the number of C:O groups or the molecule begins to absorb light of much smaller frequencies. As it will be shown later, precisely the same alterations that are responsible for the above transitions are also responsible in making the molecules more and more anisotropic.

3. The optical anisotropy of organic compounds

Extensive studies of the scattering of light by organic vapours and liquids have been made during the last seven years at Calcutta.[8] It is a well-known phenomenon that light scattered by a liquid or vapour, in a direction transverse to the direction of incidence is imperfectly polarised. The degree of polarisation can be easily determined by means of a double image prism and a nicol. r the ratio of the weak to the strong component of polarisation in the transversely scattered beam is known as the depolarisation factor of the substance. Lord Rayleigh has shown that in the case of a gas or vapour at low pressures

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

for an anisotropic molecule where A, B, C represent the moments induced in the molecule by unit electric force acting along its principal directions. The expression vanishes when $A = B = C$, in other words when the molecule is optically isotropic. The depolarisation factor r is thus a measure of the optical anisotropy of the molecule. In the gaseous state the molecules are oriented at random and their mutual influence becomes negligible. Under these conditions r is determined exclusively by the true optical anisotropy of the molecule. In a liquid, however, the influence of the surrounding molecules also modifies the effect, the actual expression for r involving the compressibility of the liquid and other factors. We shall here therefore confine ourselves to the data of light-scattering obtained with substances in the state of vapour. Some typical results from Ramakrishna Rao's paper are collected in table II.

The data show clearly an outstanding difference between the aliphatic and the aromatic classes of organic substances. The value of r, the depolarisation factor, is much larger in the case of aromatics than in the case of aliphatics which means that the aromatic structure is in general more anisotropic optically than the aliphatic structure. The values of r given in columns 2 and 4 are very significant,

[8] K S Krishnan, *Philos. Mag.* 1925 L 687.
A N Banerji, *Indian J. Phys.* 1927 VII Part I 51.
I Ramakrishna Rao, *Ibid*, p. 61.

Table II. Data of optical anisotropy

	Aromatics		Aliphatics	
Substance	(for vapour) $r \times 100$	Substance		(for vapour) $r \times 100$
Benzene	4·2	Carbon tetrachloride		0·50
Toluene	4·6	n-Hexane		1·21
Chlorobenzene	4·58	Heptane		1·40
Bromobenzene	4·83	Isopropyl alcohol		1·30
Nitrobenzene	5·6	Octane		1·66
O. Nitrotoluene	4·80	Allyl alcohol		2·58
M. Nitrotoluene	5·25	Trimethyl carbinol		0·69
Aniline	5·63	Bromoform		2·90
Pyridine	4·5	Chloroform		1·76
Naphthalene	7·9	β-Isoamylene		2·22
Quinoline	7·87	Diethyl ketone		3·18

for the anisotropy of a substance becomes extremely pronounced with increasing values of r. A depolarisation factor of 10% means that the optical polarisability in one direction is nearly 4 times than in others. Thus in the very structure of an aromatic compound is implied a high degree of molecular anisotropy. Certain types of modifications introduced into its structure, produce a still higher optical anisotropy accompanied by a development of colour. Further, it is also clear that in the aliphatic series, normal saturated compounds like hexane, heptane and octane have very moderate values for r whereas diethyl ketone, allyl alcohol, β-isoamylene and bromoform show a comparatively strong anisotropy. Diethylketone is characterised by a C:O group, whereas allyl alcohol and β-isoamylene contain the C:C group. Bromoform has three heavy atoms in the molecule as against the fourth hydrogen atom which is comparatively much lighter. It is very significant that these are the same groups which according to Sikhibhushan Dutt produce 'molecular strain'. Thus the particular groups are at work even in aliphatic molecules but the general disposition of the atoms in the latter is such that they become more or less symmetrical and the structure has not yet developed a sufficient degree of anisotropy to display its full effect.

In the aromatic series, the NO_2 and NH_2 groups stand out prominently. Nitrobenzene, nitrotoluenes and aniline have much larger values for their depolarisation factors. In other words these two groups tend to make the molecule highly anisotropic. Incidentally it may be remarked here that these two groups are also well known to colour chemists; the former as an important chromophore and the latter as an auxochrome. Nextly, a marked increase, as we pass on from benzene to naphthalene or from pyridine to quinoline is observed. Naphthalene is known to contain two condensed benzene nuclei and quinoline

stands in a similar relation to pyridine. Thus with increasing benzene rings we obtain molecules more and more optically anisotropic.

In addition to the data given in the table, two more compounds need a special mention here, namely CS_2 and CO_2. The depolarisation factors are 10·7 and 9·7 respectively which are surprisingly large. This appears to fit very well with the fact, well known to colour chemists, that C:O is a chromophore and C:S even a stronger one.

Cases are known of coloured organic compounds, as for instance, dimethyl fulvene which contain no benzene nucleus. It may be pointed out however that this substance possesses a quinonoid structure with a system of double bonds which must make it optically anisotropic. Thus if it is postulated that any structure which favours the development of a high degree of optical anisotropy also favours a development of colour, then there would be no difficulty in understanding why fulvene and other compounds of which it is a representative exhibit marked colour.

4. Electrical anisotropy of organic compounds

Substances in the gaseous or liquid state, when placed in an electrostatic field exhibit a feeble birefringence. The molecules are assumed to possess an intrinsic optical anisotropy, and hence owing to the orientative action exerted by the electrostatic field the fluid behaves as if it were a doubly refracting crystal. All substances which possess electrically polar molecules are found to have comparatively large electric birefringence as against non-polar molecules which show a very feeble effect. Born explained the large value for the polar molecules by taking into account the permanent electric doublet present therein. For non-polar molecules, the expression for K, the Kerr constant, which is a measure of the electrical birefringence, involves the optical and the electrical anisotropy of the molecule. The available data regarding the Kerr constant for organic compounds which are however, very scanty, are collected in the following table. Only non-polar molecules are given and they illustrate one or two important points.

Table III. Data of electrical birefringence

Aliphatics		Aromatics	
Substance	Kerr constant $\times 10^7$	Substance	Kerr constant $\times 10^7$
Pentane	0·05	Benzene	0·593
Isopentane	0·05	m. Xylene	0·858
CCl_4	0·074	p. Xylene	0·73
Hexane	0·056	Toluene	0·75

All aliphatics as before, are very feebly birefringent when compared to the aromatics, which indicates that the electrical anisotropy and optical anisotropy of the former class of compounds are very weak in comparison with those of the latter. CS_2 liquid gives a large electrical birefringence, its Kerr constant being 3.226×10^{-7}. This is far greater than any of the substances given in the table and indicates a high degree of electrical anisotropy for the compound in addition to the high optical anisotropy mentioned in the preceding section.

5. Magnetic anisotropy of organic compounds

Cotton and Mouton observed that liquids exhibit birefringence in a strong magnetic field and the generally accepted explanation of the phenomenon is that the molecules which are optically and magnetically anisotropic, are oriented in a magnetic field and the liquid as a whole exhibits birefringence. The magnitude of the effect depends on the extent to which the molecules are magnetically and optically anisotropic. Strongly anisotropic molecules like the derivatives of benzene and naphthalene show a highly developed magnetic birefringence, while in most aliphatic substances, the effect is very feeble though measurable, as has been shown recently at Calcutta.[9] The studies of magnetic birefringence reveal the degree of molecular anisotropy. In the following table the relative values with nitrobenzene $= 100$ are given as obtained by Cotton and Mouton for a number of liquids with which we are concerned here.

Table IV. Data of magnetic birefringence

Aromatics		Aliphatics	
Substance	C_m	Substance	C_m
Benzene	23·3	Chloroform	−2·8
Nitrobenzene	100	Bromoform	−6·8
Benzonitrile	39·5	Acetone	1·6
Phenyl butylene	64	Nitromethane	3·6
Benzophenone	57·2	Methyl iodide	−2·9
a-naphthonitrile	166	Methylene iodide	−12·3
a-chloronaphthalene	108	Isoprene	2·7

C_m represents the Cotton–Mouton constant. The same conclusions as arrived at from the data on light scattering can be drawn from this table. The aliphatics are as a class practically isotropic whereas the aromatics are strongly anisotropic.

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[9]M Ramanadham, see the preceding paper in this Journal.

In both the sections, the influence of the substituent groups is quite marked. As we pass from chloroform to bromoform and from methyl iodide to methylene iodide, the molecules are loaded more and more unsymmetrically and there is a corresponding increase in the magnetic birefringence. Isoprene illustrates the result of unsaturation. In the aromatics the effect of unsaturation as in phenyl butylene, the introduction of a C:N group as in benzo- and naphthonitriles and that of NO_2 group as in nitrobenzene is quite clear as before. Although two benzene nuclei are sufficient in themselves to give a high value as in the case of chloronaphthalene, the introduction of a C:N group makes it very marked in the case of naphthonitrile. Thus the same structures and groups that are instrumental in lowering the absorption frequencies as evinced by the data on absorption spectra, are also responsible for a large molecular anisotropy.

6. Birefringence in the crystalline state

The molecules which display a large optical anisotropy in the vapour state should necessarily exhibit a large double refraction in the crystalline state except in special cases when the effective double refraction is diminished by a special type of arrangement of the molecules in the unit cell. With a view to get a clearer understanding of the same, the optical properties of some fundamental organic substances in the crystalline state have been investigated. These together with the data already available, are given in the following table.

Table V. Crystalline birefringence

Aromatics		Aliphatics	
Substance	$n_1 - n_2$	Substance	$n_1 - n_2$
Picric acid	0·4	Hexabromethane	0·12
Picramic acid	0·45	Oxalic acid	0·18
Ammonium picrate	0·4	Aminoacetic acid	0·16
Naphthalene	0·499	Melamine	0·38
Anthracene	0·61	d. Tartaric acid	0·11
Quinone	0·34		
3. Aminoquinoline	0·36		

n_1 and n_2 represent the maximum and minimum refractive indices of the crystal.

This table again brings out the differences between aliphatics and the aromatics clearly. Of the data available in the aliphatic crystals, a few prominent ones are collected and with the exception of melamine, all of them are feebly birefringent when compared with the aromatics. Melamine has two C:N groups

and hence the increased birefringence is quite in accordance with the foregoing views. Amongst the aromatics picric acid, a well known dye, and its derivatives show fairly large birefringence. The molecule consists of three NO_2 groups substituted in a benzene nucleus. Both naphthalene and anthracene, typical representatives of the polynuclear parent substances used in the dyeing industry, exhibit high optical anisotropy. Anthracene crystals are more strongly birefringent than naphthalene crystals.

The absorption spectra of naphthalene and anthracene in the crystalline state have been obtained and the absorption maximum for anthracene is not far from the visible region whereas for naphthalene it is still in the ultraviolet. Thus it is clear that increasing optical anisotropy is a phenomenon running parallel with strong absorption and development of colour.

7. The optical basis of the quinonoid theory

One of the most prominent amongst the older theories, which resulted in a vast amount of synthetic research, was the quinonoid theory. For a detailed discussion, a reference should be made to Watson's book.[10] The theory postulates that all coloured substances are characterised by a peculiar structure known as the quinonoid structure. When a transformation takes place from the colourless leuco base, which is supposed to possess no quinonoid structure, to the coloured dye base, then the production of colour is explained by assuming that the configuration of the linkages in the molecule is so changed as to bring about a quinonoid structure. The same transformation is seen in its simplest form in the oxidation of hydroquinol to quinone.
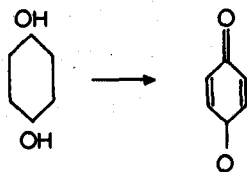
Hydroquinol has a simple benzene nucleus and is quite colourless. Quinone is representative of the paraquinonoid structure and has a rich golden yellow colour. If the postulated hypothesis is correct, in this transformation, one can expect to find a large increase in the optical anisotropy as they are typical structures characterising the colourless leuco base and the coloured dye base.

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[10]*Loc. cit.*

Data[11] available show that hydroquinol crystallises in two modifications. The principal refractive indices for the trigonal variety have been given as 1·6325 and 1·6262 for the D line. This gives hardly any birefringence and thus makes the crystal practically isotropic. Quinone, obtained by sublimation in thin flakes, is of a golden yellow colour and shows a much higher degree of optical birefringence. The difference between its principal refractive indices, as given before is about 0·34 which is many times more than that of hydroquinol. We thus see that while hydroquinol is colourless and practically isotropic, quinone a golden yellow coloured substance is highly birefringent. This is a specially good illustration of the relations existing between chemical structure and the two optical characters of colour and optical anisotropy respectively. The facts on which the "quinonoid theory" of colour is based fit in equally with the views advanced in the present paper.

8. The common origin of colour and optical anisotropy

The empirical relationships traced in the foregoing pages between absorption spectra and the molecular anisotropy of carbon compounds must naturally have some theoretical basis. To make this clear we may, at first, draw attention to some facts concerning the molecular refractivities of different classes of organic compounds.

Table VI. Molecular refractivities of organic compounds

Substance	M_d	Substance	M_d
C_6H_6		$C_6H_8N_2$	
Benzene	26·18	Adipyl dinitrile	31·14
Dipropargyl	25·60	m-phenylenediamine	34·94
		2, 5-dimethylpyrazine	32·07
$C_7H_{14}O$		Phenylhydrazine	34·01
Heptaldehyde	33·95		
p-Hexahydrocresol	33·46		

In Table VI are given a few typical data for molecular refractivity computed from the figures given in the International Critical Tables for three groups of compounds each having the same molecular formula but very different chemical constitution. Dipropargyl, adipyl dinitrile and heptaldehyde are open chain compounds whereas the others in the list are all cyclic compounds. It will be seen

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[11]Groth *Chem. Kristallogr.* Vol. 4, p. 86.

that in spite of the enormous differences in the structure, the molecular refractivities in each group of compounds show only moderate differences. We have a quite different position when instead of the molecular refractivity computed from the index for the liquid which represents an optical property of the molecule averaged for all orientations in space, we consider the same property of the molecules along different axes in its structure.

Taking the latest value[12] of r for benzene vapour as 0·042, on calculation we find that the ratio of the moment induced for vibrations in the plane to the moment for vibrations perpendicular to the plane of the benzene ring is 1·95:1, i.e., nearly twice as large in one case as in the other. In the case of aliphatic compounds, taking n-hexane as an example which has $r = 0·012$, the maximum and the minimum optical polarisations are in the ratio 1·34:1, and therefore much less different from each other. Since the average molecular refractivity depends to a much less extent on structure than these figures indicate, we are obliged to conclude, that in the cases of the aromatic compounds, the existence of a high degree of optical anisotropy involves a greatly *increased* optical polarisability or refraction in certain directions, with *per contra* a diminished optical polarisability or refraction in other directions.

A similar phenomenon is noticed in respect of magnetic anisotropy of organic compounds. Pascal showed that except for certain comparatively minor structural influences, the diamagnetic susceptibility of organic compounds did not deviate greatly from additive relationships. But when the directional properties are studied, the whole subject takes an entirely different aspect. As has been shown in another paper[13] appearing in this journal, organic crystals of the aromatic class display an astonishingly large magnetic anisotropy, the susceptibility of naphthalene crystals, for example, being nearly four times as large in one direction as in another. This indicates that while the susceptibility averaged over all directions is not very different for aromatic and aliphatic compounds, the susceptibility along a particular axis of the molecule is very much *increased* in the former class of substances with *per contra*, a diminution in other directions.

The influence of optical anisotropy is also clearly seen when it is attempted to connect refraction and dispersion data with the characteristic frequencies of absorption of the substance on the basis of the electron theory of dispersion. Drude calculated the number of electrons in several organic and inorganic compounds from the natural dispersion and arrived at the conclusion that the number present in a molecule is equal to the number of the valency electrons. Similar calculations have been made by Erfle for a number of aromatic and other unsaturated compounds, wherein he found that the number of dispersion

[12]I Ramakrishna Rao, *loc. cit.*
[13]S Bhagavantam, see preceding paper in this Journal.

electrons calculated falls short of the valency electrons to a large extent. This can be seen from the table given below in which a few typical aromatic substances are collected.

Table VII. Valency and dispersions electrons

Substance	Benzene	Toluene	Xylene	Naphthalene
v	30	36	42	48
ρ	12	14·8	17·6	13·9

v is the number of valency electrons actually present and ρ is the number deduced from the dispersion. It appears as though several of the valency electrons are out of action. Later, Richardson[14] discussed the data for magnetic rotary dispersion on the basis of electron theory and found similar discrepancies in the aromatic and unsaturated compounds. A few typical cases are collected in the following table.

Table VIII. Valency and magnetic dispersion electrons.

Aliphatics			Aromatics		
Substance	v	ρ	Substance	v	ρ
Methyl alcohol	10	10	Benzene	30	16·6
Ethyl „	16	14·6	Triphenyl methane	92	49·5
Acetaldehyde	14	13·6	Diphenyl	58	29·7
Propaldehyde	20	19·1	Orthoxylene	42	27·3
Acetic acid	16	16·7	L. Monobrom naphthalene	48	27·1

v and ρ have the same significance as before. In aliphatics there is a fair coincidence whereas in aromatics the number calculated is far lower than the actual number present. At first sight, these figures suggest that a great many of the valency electrons are ineffective. It must however be remembered that in these calculations the electron is assumed to have a symmetrical binding with the atoms or in other words, its characteristic frequency is assumed to be the same for all directions of vibration. There is no *a priori* reason for this assumption. In fact, J J Thomson[15] assumed, in order to explain the observed optical anisotropy of molecules, that the electrons in them are so bound that the characteristic

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[14]S S Richardson, *Philos. Mag.* (1916), **31**, 454.
[15]Sir J J Thomson, *Philos. Mag.* (1920), **40**, 395.

frequencies of vibration and therefore also the displacements of them produced by an impressed periodic force are different along each of three perpendicular axes fixed in the molecule. It is likely that if dispersion data along different axes in aromatic crystals such as naphthalene or anthracene are obtained and discussed, the apparant anomalies indicated in Tables VII and VIII will receive an adequate explanation.

If the cause of optical anisotropy is that assumed by J J Thomson and referred to above, it follows that molecules which are highly anisotropic and therefore very strongly polarisable in certain directions by an incident field of force must have correspondingly low characteristic frequencies of electron vibration for such directions. This is just what is necessary to explain the observed correlation between colour and optical anisotropy, and would at the same time make intelligible the apparent defect in the number of "dispersion electrons" in such molecules. Dispersion is determined to a much larger extent than refraction by the existence of relatively low characteristic frequencies, and if the latter are confined to only one out of the three optical axes of the molecule, the result would be the same as if only one-third of the electrons actually present and taking part in dispersion were effective.

It is interesting also to notice that the existence of different characteristic frequencies for different directions of vibration is also indicated by an entirely different line of thought. Silberstein[16] has shown that the mutual electrostatic influence of neighbouring isotropic atoms in a molecule should result in the molecule as a whole becoming optically anisotropic, and at the same time cause its characteristic frequencies to *diminish* in *axial* directions and *increase* along *transverse* directions.

9. The significance of pleochroism

The remarks made in the preceding section make it possible to understand why pleochroism is so frequently observed in highly coloured crystalline organic compounds. Pleochroism stands in the same relationship to ordinary light absorption that birefringence has to ordinary refraction, and according to the theoretical considerations indicated by J J Thomson and L Silberstein is more or less inevitable in highly anisotropic crystals which exhibit colour. Groth gives qualitative descriptions of the distinct pleochroism exhibited by a great number of crystals of the aromatic series in the visible region. From these, some examples of strongly coloured bodies which exhibit pleochroism are collected in the following table.

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[16] L Silberstein, *Philos. Mag.* (1917) **33**, 521.

Table IX

Substance	Pleochroism
Indigo	Very strong
Hexamethyl p. Rosaniline	Deep violet colour with strong pleochroism
	Surface is copper red
Brilliant green	Strong, sulphur yellow to currant
Azobenzene	Strong, red to citron yellow
Isatin	Strong, orange yellow to brown
Azotoluene	Marked

It is noteworthy that the majority of strongly pleochroic substances belong to the polynuclear aromatics and those few which possess one benzene nucleus and yet exhibit the phenomenon are generally characterised by either one or more NO_2 groups or a quinonoid structure.

Pleochroism and birefringence both depend on the dispersion electrons and their natural frequencies. Since however birefringence is determined also by the characteristic ultraviolet frequencies of the molecule which do not affect the absorption in the visible region, we should not expect strongly birefringent crystals always to show strong pleochroism or *vice versa*. For instance, azobenzene crystals which show marked pleochroism are only feebly birefringent whereas picric acid, which is strongly birefringent, shows weak pleochroism. The relationship between pleochroism and birefringence may also be complicated by the presence of anomalous dispersion in the visible region of the spectrum. In view of these remarks, we cannot expect any simple universal rules connecting either the principal directions of light absorption and of birefringence or their absolute magnitudes. Nevertheless, it is interesting to note, that in nine out of a dozen organic compounds exhibiting pleochroism for which complete refraction data are available, the direction of maximum optical polarisability in the crystal and of the strongest light absorption coincide. From the data given by Groth,[17] it seemed azobenzene was an exception to this rule and in view of its importance, certain qualitative observations have been made with the crystals and the results are in disagreement with those given by Groth. The crystal appears citron yellow for vibrations parallel to the b-axis and red for vibrations perpendicular to the same; its behaviour is thus quite in accordance with the general rule indicated above.

We have not at present clear-cut notions as to the actual mechanism of light absorption in solids or liquids. In the formal equations of the electromagnetic theory the term of absorption arises because the medium is supposed to possess

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[17]Groth, *Chem. Kryst* **5**, p. 60.

an electrical conductivity ρ in addition to the dielectric constant ε. The electric currents thus arising from conduction produce heat, the energy of which comes from the absorbed portion of the incident radiation. In other words, the substance behaves as an actual conductor for vibrations in the neighbourhood of its characteristic absorption frequencies. There are two alternatives possible. The first alternative is that the electron might pass out into a state of higher energy, still remaining within atomic restraints, thereby absorbing part of the incident energy, and then revert back to the former state by collisions with the surrounding atoms, which carry off the energy as thermal agitation. The second possibility is that the electron may actually be detached from the atom and carry off the energy in kinetic form. The first alternative seems to be more probable, but in this connection the work of Gudden and Pohl[18] is very significant. They found that all crystals which have a refractive index greater than 2, develop when exposed to light, a photoelectric current which is of two kinds: (1) a primary current due to photo electrons which the light has liberated from the atoms of the crystal, (2) a secondary current representing the motion of the positive ions towards the cathode, but if the excitation is caused under suitable conditions, the effect was found to be entirely due to the first cause. Later Kurrelmeyer[19] investigated the photoconductivity of sulphur crystals which has for its principal refractive indices (for the red K line) $n_\alpha = 1\cdot93$, $n_\beta = 2\cdot00$, $n_r = 2\cdot19$, and arrived at certain very interesting results. Thus it appears that all crystals with $n > 2$ generally display this phenomenon of photoconductivity, the mechanism of which is somewhat analogous to that of absorption. This supports the view that absorption or colour is a phenomenon closely allied to high refraction and birefringence. In the organic world one meets with highly birefringent crystals with one or other of the principal refractive indices greater than 2. It is likely that these display differences in photoconductivity in different directions, an effect which could not be detected in sulphur by Kurrelmeyer.

[18] Gudden and Pohl, Z. Phys. (1923) **17**, 331.
   Gudden and Pohl, Naturwissenschaften (1923) **11**, 351.
   Gudden and Pohl, Phys. Zeit. (1925) **26**, 481.
[19] Bernhard Kurrelmeyer, Phys. Rev. (1927) **30**, 893.