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APPLICATIONS IN CHEMISTRY OF PROPERTIES INVOLVING
MOLECULAR POLARISABILITY

R. J. W. Le FÈVRE



The Royal Society of New South Wales



A handwritten signature in dark ink, appearing to read 'R. J. Wood Le Fèvre', with a long horizontal flourish extending to the right.

Raymond James Wood Le Fèvre

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RAYMOND JAMES WOOD LE FÈVRE 1905-1986

Raymond James Wood Le Fèvre was born in North London on 1 April 1905. He was educated at St. James School, Twickenham, the Salesian school at Farnborough, Hants, and then at the Isleworth County School in Middlesex during the period 1916-1923. He won a Middlesex Senior County Scholarship that took him to East London College (now Queen Mary College) of the University of London. In 1925 he graduated with First Class Honours in Chemistry, and then, with a DSIR Scholarship, he began research with Eustace Ebenezer Turner* on the aromatic substitution reactions of diphenyl compounds. This, and studies of the chirality of hindered diphenyls earned him his M.Sc. degree in 1927. Le Fèvre was appointed as a lecturer in organic chemistry at University College London in 1928, and graduated Ph.D. that same year. He continued research on directive effects in aromatic substitution, but from 1933 his research began to be focussed on the measurement and application of dipole moments: he wrote a book 'Dipole Moments, their Measurement and Application in Chemistry', Methuen (London, 1938). Le Fèvre was awarded the D.Sc. degree by University College in 1935, and was promoted to Reader in 1938. At this time, he and his wife Catherine (a chemistry graduate of University College, and subsequently awarded the D.Sc. degree in 1960) began work on the Kerr effect, electrically induced double refraction, but when war broke out in 1939 this work was interrupted.

Late in 1939 Le Fèvre was given temporary release from University College for attachment to the Ministry of Home Security to be involved with the training of Gas Identification Officers; for this purpose he was located at Battersea Polytechnic for several months. Early in 1940 he joined the Directorate of Scientific Research in the Air Ministry where he advised RAF Command on chemical armaments. About a year later he was given the honorary rank of Wing Commander and sent to Singapore via West Africa, Egypt, India, Burma and Malaya to act as chemical adviser in the supply and storage of chemical weapons, and also to deal with anti-gas defence for the R.A.F. He was ordered to supervise the destruction of 'gas' stocks before the Japanese invasion, and left Singapore just in time. He arrived in Fremantle in March 1942 and remained in Australia for nineteen months, being temporarily seconded to the RAAF in the Directorates of Armament and Air Staffs Policy. He returned to the United Kingdom in December 1943 and worked at the Ministry of Aircraft Production Headquarters as an Assistant Director (Research and Development, Armament Chemistry) until the end of the war. In 1945 he was appointed as Head of the Chemistry Department at the Royal Aircraft Establishment, Farnborough.

In 1946 Le Fèvre was appointed as Professor Chemistry and Head of the Chemistry School at the University of Sydney, and he held that position until he retired in 1970. His research, sometimes in collaboration with his wife Catherine, was mainly concerned with the measurement of the dipole moments and the Kerr constants of a great variety of organic

* Turner was a Lecturer in Chemistry at the University of Sydney during 1919-1921, and it is Turner who is credited with founding the Sydney School of Coordination Chemistry - see G.J. Burrows, Liversidge Research Lecture No. 3.

compounds. He also studied the magnetic birefringence of diamagnetic compounds - the Cotton-Mouton effect.

Raymond Le Fèvre was President of Section B (Chemistry) of the Australian Association for the Advancement of Science (ANZAAS) in 1955, and President of the Royal Society of New South Wales in 1961. He was also very actively interested in the history of chemistry: he lectured on this topic to undergraduates, and, *inter alia*, contributed a chapter 'The Establishment of Chemistry within Australian Science' to *A Century of Scientific Progress*, the centenary volume of the Royal Society of New South Wales, which was published by that Society in 1968.

Honours and Awards

- 19?? Fellow, Royal Institute of Chemistry (date not available)
- 1946 FRACI (Fellow of the Royal Australian Chemical Institute)
- 1952 H.G. Smith Memorial Medal, RACI
- 1953 Coronation Medallist
- 1954 FAA (a foundation Fellow of the Australian Academy of Science)
- 1959 FRS
- 1960 Liversidge Research Lecture, Royal Society of New South Wales
- 1962 Fellow, Queen Mary College, London
- 1967 Masson Lecture, ANZAAS
- 1968 Chemical Society (London) Lecturer for Australia

Biographical Sources

1. Aroney, M.J. and Buckingham, A.D., 'Raymond James Wood Le Fèvre 1905-1986', *Historical Records of Australian Science*, 1988, **7** (3), 273-297.
2. Aroney, M.J. and Buckingham, A.D., 'Raymond James Wood Le Fèvre 1 April 1905-26 August 1986: elected F.R.S. 1959,' *Biographical Memoirs of Fellows of the Royal Society*, 1988, **34**, 373-403.

Scientific Publications by R.J.W. Le Fèvre

Le Fèvre was the author / co-author of some 440 research papers, and about 30 other publications including books, chapters in books, lectures, historical and biographical articles. These are listed in full as appendices to the biographical articles (1) and (2) quoted above.

APPLICATIONS IN CHEMISTRY OF PROPERTIES INVOLVING MOLECULAR POLARISABILITY*

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Introduction

Mr. President Ladies and Gentlemen,

Before saying anything else I want to thank the Council of the Royal Society of New South Wales for the honour they have conferred on me by the invitation to give this lecture. I am especially appreciative because I am the first of Liversidge's successors to be so favoured. After nearly fourteen years in Australia my admiration of the part which Archibald Liversidge quietly took in the chemical and scientific life of this country and this University continues to grow. His achievements have been recorded by Sir Edgeworth David in 1931 and, more recently, by Professor Mellor in 1957; between the lines one can feel the difficulties, the "limitations and misunderstandings", against which he worked, yet he built a new chemistry department here, supported the introduction of women students, persuaded the University to set up a Faculty of Science (of which he became first Dean), was prominent in the inauguration of technical education in N.S.W., was a founder of A.N.Z.A.A.S., was a reviver and supporter of this Society, and was active in researches on chemical mineralogy, on the origin and precipitation of gold, on the compositions of rocks and ores and meteorites - researches of peculiar appropriateness to the Australia of his day.

Mellor says: " In some ways Liversidge was ahead of his time." Perhaps he foresaw how chemistry would change and expand. By his Will he founded this Research Lectureship, and three others for a similar purpose elsewhere. His directions show his far-sightedness: the "lectures are to be open to the public (free or at a nominal fee), but are not to be popular lectures nor such as are intended for the ordinary lecture room instruction of undergraduates, but shall be such as will primarily encourage research and stimulate the research instead of merely giving instruction in what is already known". In satisfaction of these terms, previous Liversidge Lecturers have usually selected subjects with which they themselves are personally connected. I propose to do likewise.

Genesis of the Subject - As a young organic chemist in England during the late 1920's, I saw and heard a great deal of the then developing theoretical approaches to reactivity and reaction mechanism associated particularly with the names of Robinson and Ingold - approaches which fundamentally involved the concepts of permanent and temporary polarity, that is, of polarisation and polarisability, and their influences on and within molecules. The physical measurement of the former I took up partly from stereochemical motives and partly

*Liversidge Research Lecture delivered before the Royal Society of New South Wales, October 13th, 1960. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1961, **95**, 1-11.

as a contribution to quantitative knowledge of the "inductive" and "mesomeric" effects. Much less was known of the "tautomeric" or "inductomeric" polarisability effects; accordingly, a few years before the last war, my wife and I decided to attempt their direct investigation. This necessitated the practical measurement of electric double refraction and thus brought us into contact with a physical property which, during our period in Australia, has been developed into stereochemical usefulness, and which is now beginning to be applied by others elsewhere in the world.

The Anisotropy of Molecular Polarisability

Nearly all molecules are anisotropically polarisable under an electric field. The degree of such anisotropy is sensitively connected with molecular structure, conformation, and morphology; its measurement and interpretation are therefore the basis of the developments just mentioned.

When an electric field of unit strength acts upon a molecule the dipole moment induced is, by definition, the polarisability b of the molecule. With spherically symmetrical molecules the directions of action of b and of the field will be always collinear; with less symmetrical molecules the induced moment will usually be at angles to the field depending on the orientations of the molecule in the field - in other words, the field will induce component moments parallel and perpendicular to itself. Only for certain clearly definable orientations will these perpendicular components be zero. In the case of a completely unsymmetrical molecule there will be three such orientations, mutually at right angles, and the moments induced parallel with the field in each situation are known as the principal polarisabilities b_1 , b_2 , and b_3 of the molecule.

These polarisabilities enter the mathematical treatments accorded by Langevin, Gans, Born, Debye and others to many optical and electrical phenomena, and in particular to refractivity, light scattering, dielectric polarisation and the Kerr effect. For a given molecule, b_1 , b_2 and b_3 are therefore accessible from quantitative measurements associated with the phenomena named. Details are given in a review by Le Fèvre and Le Fèvre (1955). Thus the total $(b_1+b_2+b_3)$ comes from molecular refractions, the squares of the differences

$$(b_1-b_2)^2 + (b_2-b_3)^2 + (b_3-b_1)^2$$

from depolarisation factors in Rayleigh scattered light, and a sum $(\theta_1+\theta_2)$ from the observed Kerr constant B (defined as $(n_p-n_s)/\lambda E^2$, where n_p and n_s are the refractive indices of a dielectric parallel and perpendicular to the lines of force of a field E , for light of wavelength λ). Expansions of θ_1 and θ_2 are:

$$\theta_1 = [(b_1-b_2)^2 + (b_2-b_3)^2 + (b_3-b_1)^2]DP / 45kT (EP)$$

$$\theta_2 = [(b_1 - b_2)(\mu_1^2 - \mu_2^2) + (b_2-b_3)(\mu_2^2 - \mu_3^2) + (b_3 - b_1)(\mu_3^2 - \mu_1^2)]45k^2T^2$$

(μ_1 , μ_2 , and μ_3 being the resolutes of the resultant molecular moment along the directions in which b_1 , b_2 , and b_3 are measured, and DP and EP the distortion and electronic polarisations respectively).

Application to Solutes - The underlying theory upon which these formulae are based applies strictly to dielectrics as gases - a state into which many interesting substances cannot be brought without decomposition and in which all the measurements involved are practically

difficult. Accordingly, our first task was to develop and test methods for working with substances in solution. This phase was concluded for the Kerr effect by 1953 (Le Fèvre and Le Fèvre) and for light scattering by 1957 (Le Fèvre and Purnachandra Rao). Procedures now exist whereby "molar Kerr constants" and "molecular anisotropies", given *for gases* by

$${}_m K = 6Bn\lambda M / (\epsilon + 2)^2 (n^2 + 2)^2 d$$

$$\text{and } \delta^2 = 10\Delta / (6 - 7\Delta)$$

$$= [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] / (b_1 + b_2 + b_3)^2$$

(Δ = depolarisation factor,

n = refractive index,

ϵ = dielectric constant,

d = density,

M = molecular weight),

may be measured *for solutes* at infinite dilution. (The "molar Kerr constant" of a substance can be visualized as the differences of its molecular refractions parallel and perpendicular to a unit electric field in the Kerr cell.)

From the extrapolated molar Kerr constant $\infty({}_m K_2)$ and the electronic polarisation EP of a solute, we have, at 25° C,

$$\theta_1 + \theta_2 = 0.2378 \times 10^{-23} \times \infty({}_m K_2)$$

and

$$b_1 + b_2 + b_3 = 0.11891 \times 10^{-23} \times EP$$

Several hundred $\infty({}_m K_2)$'s have now been recorded (mostly in the *Journ. Chem. Soc.*) by the Le Fèvres and their collaborators, and from the majority the related principal polarisabilities calculated.

Principal Molecular Polarisabilities and Bond Polarisabilities

The data thus accumulated have further been analysed in terms of anisotropic bond polarisabilities. A suggestion that bonds may have different polarisabilities along their lengths and in the two perpendicular transverse directions was first made qualitatively in 1931 by Meyer and Otterbein. Representing these as

$$b_L^{XY}, b_T^{XY}, \text{ and } b_V^{XY} \quad (L = \text{longitudinal}, T = \text{transverse}, \text{ and } V = \text{vertical})$$

for the bond joining the atoms X and Y , we have e.g. for the molecule XY_2 where the angle YXY is 2θ :

$$b_1^{XY_2} = 2(b_L^{XY} \cos^2 \theta + b_T^{XY} \sin^2 \theta),$$

$$b_2^{XY_2} = 2(b_L^{XY} \sin^2 \theta + b_T^{XY} \cos^2 \theta),$$

$$\text{and } b_3^{XY_2} = 2b_V^{XY}.$$

In many instances the calculations are simplified by the facts that $b_2 = b_3$ or

$b_1 = b_2$, or $b_T^{XY} = b_V^{XY}$, etc. By application to molecules of known structure of the type of argument illustrated by this simple example, the polarisabilities of the commoner bonds entering organic molecules have been deduced. They are listed in Table 1.

As is to be expected, the anisotropy of a given bond is not a "universal" constant but appears to be somewhat affected by the structural environment; such becomes notably the case when double bonds are in conjugation - signs of this can be seen in the data for the aryl halides, and will often be found for links in molecules markedly exhibiting exaltations of refractivity. Perhaps part of the inconstancy is due to the incorporation into the listed values of "secondary polarisabilities" - the augmentations or diminutions caused mutually by two induced moments in proximity to one another and varying with their orientations; *a priori* estimations of such effects by the formulae of electrostatics, however, are often tediously long and always involve the unknown dielectric constant of inter-atomic space. Yet another cause could be the inclusion in bond polarisabilities of part of the polarisabilities of adjacent lone-pair orbitals - this may explain why the H-N and C-N bonds appear to have b_L less than b_1 . A safe view-point is that the data in Table 1 are empirical and should be useful in situations analogous to those from which they have come.

TABLE I

| Bond | $10^{23} b_1$ | $10^{23} b_2$ | $10^{23} b_3$ | Bond environment |
|----------------------------------|--------------------|--------------------|--------------------|---|
| C-H | 0.064 | 0.064 | 0.064 | Paraffin hydrocarbons |
| C-C | 0.098 ₆ | 0.027 ₄ | 0.027 ₄ | <i>cyclo</i> Hexane |
| " | 0.097 ₉ | 0.027 ₂ | 0.027 ₂ | <i>cyclo</i> Pentane |
| C-F | 0.12 ₅ | 0.04 | 0.04 | CH ₃ F |
| " | (0.07) | (0.07) | (0.03) | C ₆ H ₅ F |
| C-Cl | 0.31 ₈ | 0.22 | 0.22 | CH ₃ Cl |
| " | 0.39 ₅ | 0.16 | 0.16 | (CH ₃) ₃ CCl |
| " | 0.399 | 0.185 | 0.185 | CCl ₄ and CHCl ₃ |
| " | 0.382 | 0.185 | 0.185 | <i>cyclo</i> -C ₆ H ₁₁ Cl |
| " | 0.42 | 0.19 ₅ | 0.15 | C ₆ H ₅ Cl |
| C-Br | 0.46 ₅ | 0.31 | 0.31 | CH ₃ Br |
| " | 0.60 | 0.26 | 0.26 | (CH ₃) ₃ CBr |
| " | 0.53 | 0.27 | 0.27 | <i>cyclo</i> -C ₆ H ₁₁ Br |
| " | 0.62 | 0.24 | 0.22 | C ₆ H ₅ Br |
| C-I | 0.68 | 0.47 | 0.47 | CH ₃ I |
| " | 0.88 | 0.42 | 0.42 | (CH ₃) ₃ CI |
| " | 0.80 ₇ | 0.41 ₈ | 0.41 ₈ | <i>cyclo</i> -C ₆ H ₁₁ I |
| " | 0.91 | 0.53 | 0.33 | C ₆ H ₅ I |
| C=C | 0.280 | 0.073 | 0.077 | CH ₂ = CC1 ₂ |
| CC triple | 0.35 | 0.13 | 0.13 | C ₂ H ₂ |
| C-O | 0.081 | 0.039 | 0.039 | Paraldehyde |
| C=O | 0.230 | 0.140 | 0.046 | (CH ₃) ₂ C=O |
| N-H | 0.050 | 0.083 | 0.083 | NH ₃ |
| N-C | 0.057 | 0.069 | 0.069 | (CH ₃) ₃ N |
| C _{Ar} -C _{Ar} | (0.224) | (0.021) | 0.059 | C ₆ H ₆ |

Polarisability in Relation to Molecular Structure

The application of bond polarisabilities to problems involving choices of structures or conformations is straight-forward. In each of the various alternative models a convenient set of rectangular axes, x , y and z is set. One first imagines a unit field acting e.g. along x , and computes the moments b_{xx} , b_{yx} and b_{zx} which it induces in the x , y and z directions; next the process is repeated for the field along the y , and finally along the z axis. Solution of the cubic equation in λ

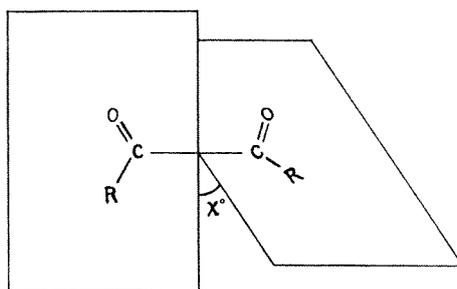
$$\begin{vmatrix} (b_{xx} - \lambda) & b_{xy} & b_{xz} \\ b_{yz} & (b_{yy} - \lambda) & b_{yy} \\ b_{zx} & b_{zy} & (b_{zz} - \lambda) \end{vmatrix} = 0$$

then yields the required principal polarisabilities, b_1 , b_2 , and b_3 for the structure under consideration, and permits the calculation of the direction cosines which locate these b 's in the axes taken.

When b_1 , b_2 , and b_3 are available from experiment, comparison can be made directly. In other cases the b 's may be used in conjunction with the observed dipole moment to predict the appropriate molar Kerr constants, which are then compared with the measured $\infty(mK_2)$. In many instances the correct model is at once obvious.

Some Specific Applications

A few qualitative and quantitative applications of polarisability to questions of molecular space-formulation were described by Le Fèvre and Le Fèvre in their 1955 *Review*. Further evidence bearing on some of these has since come forward. The skew structure assigned to benzil, because its Kerr effect was algebraically negative, is now substantiated by work recently completed by Miss P. Cureton, whose experiments show incidentally that the related diketones, furil and diacetyl, are also best represented by skew formulae:

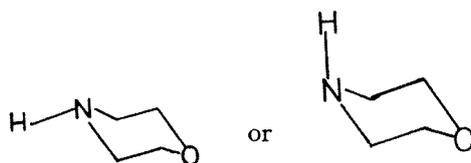


| R | Me | C ₆ H ₅ | C ₄ H ₃ O |
|-----------------------------|------|-------------------------------|---------------------------------|
| χ° | 156° | 97° | 121° |
| $10^{12} mK_{\text{calc.}}$ | -37 | -664 | -627 |
| $10^{12} mK_{\text{obsd.}}$ | -28 | -664 | -627 |

In such instances, of course, the resultant dipole moment varies with the azimuthal angle, χ° , so that in principle at least the degree of non-planarity could be determined from the polarity.

Considerations involving the anisotropy of polarisability are most useful when the choice to be made is between several configurations any one of which may be expected to have a resultant dipole moment indistinguishable from or closely similar to those of the others. Three examples of this type will be cited.

The first concerns the molecule morpholine for which theoretically a number of "boat" and "chair" structures can be written. Aroney and Le Fèvre (1958) showed that all but two can be dismissed because neither their calculated dipole moments nor their calculated molar Kerr constants approached the values from actual measurement (*viz.* 1.54 D and -24.3×10^{-12} respectively). The choice lay therefore between the two representations



$$10^{12} mK_{\text{calc.}} = +14.1 \quad \text{or} \quad -26.2$$

$$\mu_{\text{calc.}} = 1.5_1 \text{ D} \quad \text{or} \quad 1.5_1 \text{ D.}$$

and the clear-cut conclusion was that morpholine exists, as a solute, almost wholly as the conformation with the N-H link disposed *axially*.

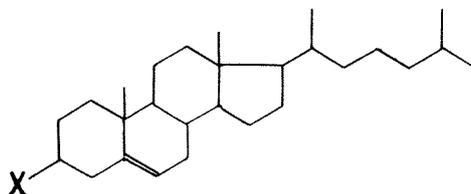
The second example concerns the related problem among the *cyclohexyl*-halides. Le Fèvre and Le Fèvre first dealt with the matter in 1956, reporting that *cyclohexyl*-chloride, bromide, and iodide appeared to have their halogens attached predominantly equatorially. Improved calculations (based on more appropriate C-X link polarisability data) published recently (Le Fèvre, Le Fèvre, Roper and Pierens, 1960) for the principal polarisabilities of the equatorial and axial isomers of $C_6H_{11}X$, together with the location of the directions of action of the molecular dipole moments within the framework defined by the coordinates along which b_1 , b_2 , or b_3 are measured, give the following results:

| X in $C_6H_{11}X$ | Attachment of C-X bond | $10^{12} \infty(mK_2)$ | |
|-------------------|------------------------|------------------------|----------------------------------|
| | | $10^{12} mK$ calc. | observed in carbon tetrachloride |
| Cl | axial | 51 | 122 |
| | equatorial | 154 | |
| Br | axial | 111 | 181 |
| | equatorial | 226 | |
| I | axial | 179 | 249 |
| | equatorial | 291 | |

Since mK observed for a mixture should be additively related to the mK 's of the components, the implication is that at infinite dilution in carbon tetrachloride these halides exist *ca.* 70%, 60%, and 60% respectively in their equatorial form. By different techniques (kinetic studies,

N.M.R. and infra-red spectra) and in other media, equatorial: axial ratios lying between 3 : 2 and 5 : 1 have been reported. The matter deserves further investigation, especially from the viewpoints of solvent and temperature effects.

The third example resembles the second but is advanced because the carbon skeleton involved belongs to the important natural class of steroids. When X = OH the adjoining formula



is that of cholesterol; we have examined *inter alia* cholesteryl chloride, bromide, and iodide, and cholestenone (in which C3 is the carbon of a ketone group). A practical difficulty needed to be removed as a preliminary: measurements of the Kerr effect are normally made in polarised light between Nicol prisms crossed for *extinction*, so that the introduction of molecules having natural optical rotatory powers prevents this condition being attained. Mr. J.M. Eckert has shown, however, that errors caused thereby diminish steadily as the concentrations (in benzene, carbon tetrachloride, etc.) of the active solute are reduced; accordingly, by a process of extrapolation the electric birefringence due to the solute can be deduced at infinite dilution. (As a check, the molar Kerr constants at infinite dilution found for a number of optical antipodes and for their corresponding (\pm) forms have been demonstrated as the same within the ordinary limits of experimental errors.)

With the cholesteryl halides our objective was to ascertain whether the links C-X were "equatorial" or "axial". As a guide to the inter-valency angles in the $C_{27}H_{45}$ - radical the X-ray analysis of cholesteryl iodide by Carlisle and Crawfoot (1945) has been invoked, and two treatments given the data thus available: (a) a scale-model built to show the locations of the numerous atom-centres and centre-centre links, and (b) direction cosines for all the anisotropically polarisable bonds calculated from Cartesian coordinates, computed in turn from position coordinates obtained by multiplying Carlisle and Crawfoot's fractional coordinates by the appropriate unit cell dimensions.

By "trial and error" - by stretching threads through the model and directly measuring angles between thread and bonds - the axes of maximum and minimum polarisability were sought empirically; later the full and lengthy calculation of the polarisability matrix (as described formally above) has been undertaken, using the SILLIAC machine in the School of Physics to solve the final cubic equation, to give the desired principal polarisabilities, and the nine direction cosines required to define their dispositions in space. Values of b_1 , b_2 , and b_3 by the two methods agree to within 1%, although the angles between C-X and b_1 differ by 8° , 6° , and 4° for the chloride, bromide, and iodide respectively (being 6° throughout when measured manually).

At the present stage the analysis is as follows

| <i>Solute</i> | $10^{12} mK$ | | |
|--------------------------|------------------|-------------|----------|
| | Calc. equatorial | Calc. axial | observed |
| Cholesteryl chloride | 360 (manual) | | |
| | 306 (SILLIAC) | -88.0 | +435 |
| bromide | 447 (manual) | | |
| | 384 (SILLIAC) | -50.9 | +492 |
| iodide | 532 (manual) | | |
| | 462 (SILLIAC) | +4.1 | +517 |
| Δ^5 -Cholestenone | +280 (calc.) | | +282 |
| Δ^5 -cholestene* | +42 (calc.) | | +44 |

*Now under examination by Mrs. S. Alamelu.

It is seen that in the three halides equatorially disposed C-X bonds are indicated very strongly, although the observed molar Kerr constants exceed those calculated by 10-25%. Reasons for the discrepancy are not clear. These molecules are the largest so far studied, they contain more than 70 bonds, so that small inadequacies in the polarisabilities of these will be summed up in the calculation of the molecular polarisabilities; moreover we may here be dealing with cases where neglected secondary effects - the polarisation induced in one link affecting that induced in its neighbours - are accumulating and becoming noticeable (yet the calc. and obsd. mK 's for Δ^5 -cholestenone and Δ^5 -cholestene are most satisfactory).

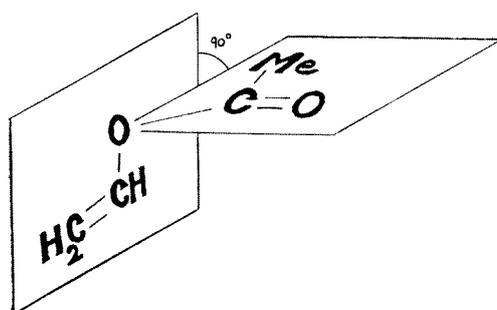
Finally, we have no evidence that a $C_{27}H_{45}X$ molecule *in solution* will be identical with cholesteryl iodide *in the crystalline state*. An analogous assumption would be misleading in certain other cases, e.g. dimethyl oxalate, diethyl terephthalate, 1,2-dibromoethane, and 1,4-dimethoxybenzene are all reported to be *trans*-forms in the solid phase (*Chem. Soc. Special Pubn.* No. 11, 1958), but their non-zero dipole moments as solutes demonstrate that they are not thus present in solution.

Nevertheless, despite the imperfections mentioned, we submit this work as the first to display the conformation at C3 of dissolved cholesteryl halides without using arguments of analogy.

Other Conformational Studies Recently Published or in Progress

Time will not permit an extensive discussion of further examples. Clearly the method is suitable for the investigation of the "apparent" or "average" configuration adopted by a flexible or easily distorted solute molecule. Cases of this type described in recent publications include the polystyrenes, polyvinylacetates, and polyethyleneglycols (with Miss G. M. Parkins and my wife, 1958 and 1960), various trialkylamines, arylamines, hydrazines, piperidines, piperazines, phenylene diamines, etc. (with M. Aroney, 1960), most of the *n*-alcohols up to octadecyl (with C.G. Le Fèvre, B. Purnachandra Rao, and A. J. Williams, 1960), neopentyl halides (with C.G. Le Fèvre and M.R. Smith, 1958), azodiformates, maleates

and fumarates (with C.G. Le Fèvre and W.T. Oh, 1957), *cycloheptanone* and other *cyclic-ketones* (with C.G. Le Fèvre and B. Purnachandra Rao, 1959), substituted diphenyls (with C.G. Le Fèvre and J. Y.H. Chau, 1959), and the mono- and di-methoxy-, -acetoxy-, and -carbethoxybenzenes (with M. Aroney and Shu-Sing Chang, 1960). In many of these instances our measurements have indicated the existence of several conformations, usually foreseeable by inspection of scale-models showing van der Waals radii and thus steric hindrances. An interesting case where results can be explained with a single form is monomeric vinyl acetate mK obsd. for which is 3.6×10^{-12} , versus values ranging from $30 - 118 \times 10^{-12}$ for the various planar forms;



$$mK \text{ obs.} = 3.6 \times 10^{-12}$$

$$mK \text{ calc.} = 4.9 \times 10^{-12}$$

here the vinyl-group seems to be conveniently oriented to obviate the acetoxy-radicals impeding the growth of the carbon chains during addition polymerisation.

Other studies now in hand concern trialkyl borates (M. Aroney and P.M. Lenthen), alkyl nitrites (K.D. Steel), monohalogeno-alkanes (A.J. Williams), $\alpha : \omega$ -dihalogeno- and dicarbethoxy-alkanes (M. Aroney and D. Izsak), anils and azo-compounds (R.S. Armstrong and N. Hacket), the di-*n*-alkyl ketones (M. Aroney and D. Izsak), isomeric oximes (N. Hacket), tropinone (J.M. Eckert), Tröger's base (M. Aroney and L.H.L. Chia), many aliphatic and aromatic hydrocarbons including rubber and gutta-percha, squalene, and other polyisoprenoids (S. Alamelu and K.M. Somasundaram), etc. The objective of all these is conformational information.

Time allows only a mention of a widening of technique now proceeding in our laboratories. By the imposition of several kilovolts, suddenly and only for fractions of a microsecond, to a solution under examination we should be able to measure Kerr effects with conducting media, and also - with natural macromolecules such as proteins - to estimate rotary diffusion constants, and hence length-diameter ratios for the solute particles concerned. Mr. Steel is developing the necessary equipment, and is intending to gather experience by an exploration of the warm-water induced reaction: collagen \rightarrow gelatine. In the hope that we shall later be able to handle, *inter alia*, nucleic acids by such methods, preliminary work by conventional procedures has been started on phosphate esters (L.H.L. Chia) and P-O bonds (N. Hacket), on a few purine derivatives (Miss P. Cureton), and on certain alkylated and acetylated sugars (J.M. Eckert). Macromolecular morphology is here the ultimate objective - many difficulties lie ahead, and the first is not the least: to make reliable electric double refraction observations in aqueous media; afterwards will come the problems of interpretation!

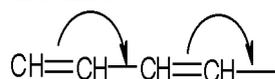
The Anisotropy of Polarisability in Conjugated Systems

That exaltations of mean polarisability occur in conjugated systems has been recognized for years through the imperfect additivity shown by their molecular refractions, R . ($R_{\text{expt.}} - R_{\text{calc.}} = \Delta R = \text{exaltation}$). It was not known, however, whether these polarisability increments occurred uniformly (isotropically) within a molecule, or preferentially (anisotropically) in particular directions. Information on the matter is obviously necessary if the fullest stereochemical use is to be made, along lines illustrated above, of polarisability as an anisotropic molecular property, calculable from the related anisotropic bond properties.

Le Fèvre and Le Fèvre first attacked the problem, as it related to substituted benzenes, in 1954. By subtracting from the principal polarisabilities found by experiment for $\text{C}_6\text{H}_5\text{X}$ and CH_3X the corresponding polarisabilities of C_6H_5 (i.e. benzene minus C-H) and CH_3 (i.e. methane minus C-H), b_L^{c-x} , b_T^{c-x} and b_V^{c-x} values for the C-X bond in the two situations were obtained. The differences, $(b_i^{cx})_{\text{aryl}}$ minus $(b_i^{cx})_{\text{aliphyl}}$, where $i = 1, 2, \text{ or } 3$, suggested that the exaltations of polarisability produced by substituents in aromatic combination were concentrated along those directions in which electromeric or hyperconjugative electronic displacements could be expected by organochemical theory; for the halogeno-benzenes this direction is coincident with $\mu_{c,x}$, i.e. the exaltation predominantly affects b_1 , often apparently at the expense of b_2 and b_3 (cf. Le Fèvre and Purnachandra Rao, 1958).

Exaltations among benzene derivatives are, however, rather small; they are much larger with open-chain conjugated systems. Examples of the latter type, recently studied by Bramley and Le Fèvre (1960), are the α : ω -diphenylpolyenes, $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_n\text{C}_6\text{H}_5$, in which $n = 1$ to 4. These materials display exaltations of mean polarisability, respectively, for $n = 1, 2, 3, \text{ and } 4$, of *ca.* 0.25, 0.59, 0.96 and 1.3×10^{-23} c.c.; their measured molar Kerr constants rise roughly by $10^{12} mK = 41 + 79n^2$, where 41 is the value for biphenyl ($n = 0$).

Of course, such molecules are probably mesomerides in which the C=C bonds lose their identities by mesomeric shifts of the kind



their π -electrons becoming part of a delocalized system. Nevertheless an analysis in which the exaltation of polarisability due to conjugation is separated from the polarisability of an "isolated" C=C bond, although perhaps unjustifiable by theory, enables us to retain the procedure of adding bond polarisabilities tensorially, and thereby to forecast mK 's in reasonable accord with those actually measured.

We first calculate b_1^* , b_2^* and b_3^* , without allowance for conjugation, using the geometrical specifications established by X-rays for these polyenes. Then, utilising the conclusion reached with the benzene derivatives, we add the exaltation of polarisability along that direction in which mesomerism is most to be expected. Finally, we recalculate b_1 , b_2 and b_3 as the maximum, intermediate, and minimum polarisabilities respectively for the real structure; from these, and for comparison with experiment, the molar Kerr constants can be easily computed.

Apart from molecular refractions, two other sources of estimating exaltations have appeared: (a) If b is the projection of the distance between the 4 and 4' positions onto an axis defined by the mid-points of the bonds in the polyene chain, and b_1^* is calculated for the "isolated" bonds alone, then

$$b_{\max} = b_1^* + kl^3$$

where k has a mean value of 1.13×10^{-2} ; l for the α,ω -diphenylpolyenes is $6.25 + 2.47n$ Å units. (b) If λ_{\max} m μ is the wave-length of maximum absorption for the K -band in a conjugated hydrocarbon, then

$$\Delta b_{\max} = b_{\max} - b_1^* = 9.762 \times 10^{-7} (\lambda_{\max} - 206)^3.$$

As an illustration, the effect of using the second equation may be shown:

| n | $10^{12} mK$ calc. (without exaltation) | $10^{12} mK$ calc. (with exaltation) | $10^{12} mK$ (observed) |
|-----|--|---|----------------------------|
| 1 | 45 | 111 | 124 |
| 2 | 62 | 358 | 357 |
| 3 | 82 | 764 | 692 |
| 4 | 105 | 1759 | 1740 |

"Corrections" by the other two routes mentioned are similar in magnitude. In general it appears that the "longitudinal" polarisability of a conjugated system is a function of the cube of its length - a prediction earlier made by Davies in 1952 from theoretical considerations.

More work is clearly needed on this important aspect of molecular polarisability. Before leaving for London last year Mr. Bramley had examined a number of conjugated ketones; his experiments are being continued and extended by Messrs. D. Izsak and M. Aroney. Discussion of them now would be premature, although it should be said that nothing to date has emerged which is in essential disharmony with the conclusions reached with the diphenylpolyenes.

Polarisabilities and Bond Lengths

Turning aside from the stereo-structural employments of polarisability, a few other aspects of interest have emerged during our work and justify a brief mention. Since by elementary electrostatics a conducting sphere of radius r placed in an electric field of intensity F acquires an electric moment of $r^3 F$ (i.e. its polarisability is r^3) it was natural to search among our bond data for relationships involving (bond-length)³.

Le Fèvre in 1958, considering the information which by then had accumulated on the principal polarisabilities of *single* bonds, observed that the *longitudinal* polarisabilities, b_L^{X-Y} , of such bonds tended to follow relationships of the type

$$10^{24} b_L^{X-Y} = A + Bd^3$$

in which A and B were constants, and d (in Ångström units) was obtained as follows: (a) when neither X nor Y is a terminal atom, $d = r_{X-Y}$ (the inter-centre distance), or (b) when Y is a terminal atom, $d = r_{XY} + r_Y$, or (c) when $X-Y$ is a diatomic molecule,

$d = r_{XY} + r_X + r_Y$ (r_X and r_Y being the radii of atoms X and Y). Two equations were proposed:

$$10^{24}b_L^{X-Y} = 0.140 + 0.156d^3 \quad \dots\dots\dots(i)$$

$$10^{24}b_L^{X-Y} = 0.106 + 0.186d^3 \quad \dots\dots\dots(ii)$$

respectively to cover the b_L 's derived from the methyl halides and those from the *cyclohexyl* halides.

Table 2 shows forecasts made by (i) and (ii).

TABLE 2
Calculations of $10^{24}b_L^{XY}$

| Bond | r_{XY} (A) | r_Y (A) | b_L by (i) | b_L by (ii) | b_L Found |
|-------------------|-------------------|--------------|------------------|------------------|--------------------------------------|
| N-H | 1.01 | 0.30 | 0.5 | 0.5 | 0.5 |
| C-H | 1.09 | 0.30 | 0.6 | 0.6 | 0.6 |
| C-N | 1.47 | | 0.6 | 0.7 | 0.6 |
| C-O | 1.43 | | 0.6 | 0.6 ₅ | 0.8 |
| C-C | 1.57 | | 0.7 | 0.8 | 1.0 |
| C-F | 1.38 | 0.64 | 1.4 | 1.6 | 1.2 ₅ |
| C-Cl | 1.78 | 0.99 | 3.4 ₅ | 4.1 | 3.2 (3.8 ^a) |
| C-Br | 1.94 | 1.14 | 4.7 | 5.5 | 4.6 ₅ (5.3 ^a) |
| C-I | 2.13 | 1.33 | 6.6 | 7.8 | 6.8 (8.1 ^a) |
| H-Cl ^b | 1.27 ₅ | 0.99 | 2.8 | 3.2 | 3.1 |
| H-Br ^b | 1.414 | 1.14 | 3.8 | 4.4 | 4.2 |
| H-I ^b | 1.604 | 11.33 | 5.4 | 6.4 | 6.6 |

^a b_L^{XY} found in cyclohexyl halides

^b r_X taken as 0.30 Å.

It is seen that predictions are fairly satisfactory. No analogous general expressions for the *transverse* polarisabilities b_T^{X-Y} have been found, but since for *single* bonds $b_{mean}^{X-Y} = (b_L^{X-Y} + 2b_T^{X-Y}) / 3$, estimates of b_T^{X-Y} are obviously accessible from bond refractivity data in conjunction with b_L^{X-Y} (calculated).

Experimental evidence on bonds of order higher than unity is scarce. It is relevant, however, that modifications of the above equations show promise. If, for example, (i) is written as (iii)

$$10^{24}b_L^{XY} = 0.140 + 0.156[d^3 + 9.5(r_{single}^3 - r_{obsd}^3)] \dots\dots\dots(iii)$$

then the following forecasts are possible with $d = r_{obsd}$.

| Bond | $r_{\text{obsd.}}$ | $10^{24}b_L$ | $10^{24} b_L$ calc. | found |
|----------------------|--------------------|--------------|------------------------|------------------|
| C=C | | 1.33 | 2.7 ₅ | 2.8 ₀ |
| CC triple | | 1.20 | 3.6 | 3.5 |
| C=O | | 1.22 | 2.1 | 2.3 |
| CO (Carbon monoxide) | | 1.14 | 2.5 | 2.6 |
| CC (Aromatic) | | 1.40 | 2.2 | ? |

Equations of type (iii) moreover may be applicable to "single" bonds shortened by mesomerism, as in the tri- and tetrachloroethylenes, where the C-Cl separations are *ca.* 1.71 Å, or in the dichloroethylenes and chlorobenzene, where they are *ca.* 1.69 Å. If, with these r_{XY} 's, d is calculated as for single bonds and inserted in (iii), longitudinal polarisabilities for C-Cl emerge which exceed by 0.7 or 0.8 x 10⁻²⁴, respectively, the value appropriate for a single bond attached to a methyl-group.

Thus, empirically at least, we find that longitudinal polarisabilities of bonds and the exaltations of polarisability of molecules can be connected with cubes of lengths.

Polarisabilities and Bond Stretching Frequencies

Another generalization deducible from Table 1 concerns a quantity Q given by

$$Q = (1 / r_{XY}^2)(b_L^{XY} / \bar{M})^{1/3}$$

in which r is the internuclear distance in the link $X-Y$, \bar{M} is the reduced mass for $X-Y$, and b_L^{XY} is in units of 10⁻²³ c.c. Straight-line relationships seem to exist between stretching frequencies ν (as cm⁻¹) and Q (see Fig. 1).

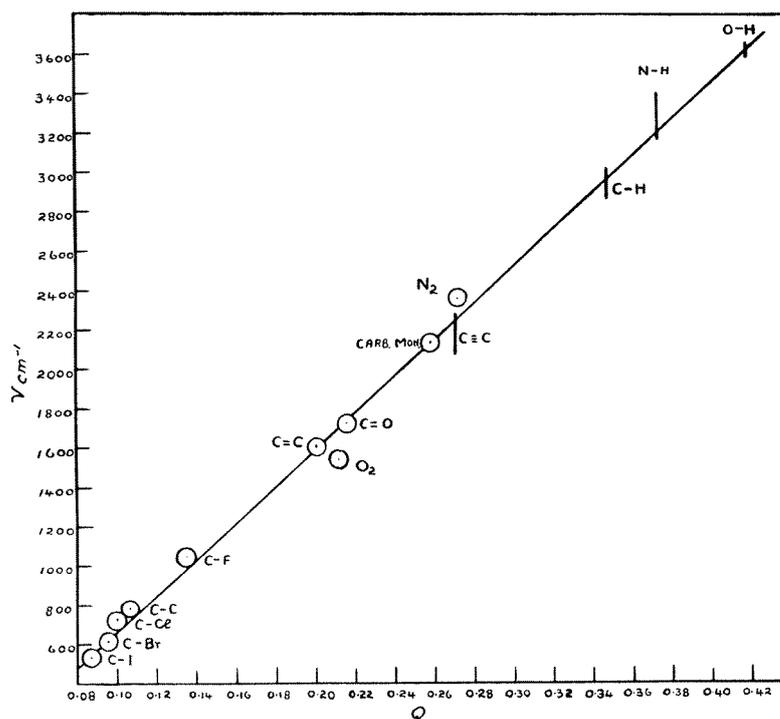


Fig. 1

TABLE 3

| Bond | ν (cm ⁻¹) | r (Å) | b_L^{XY} (calc.) | b_L^{XY} (ex Kerr effect) |
|-----------|---------------------------|---------|--------------------------|--------------------------------|
| O-H | 3650 - 3590 | 0.97 | 0.06 | ? |
| N-H | 3400 - 3200 | 1.01 | 0.06 - 0.05 | 0.05 |
| C-O | ca. 1100 | 1.43 | 0.18 | 0.08 |
| C=O | 1720 | 1.22 | 0.22 | 0.23 |
| C=N | 1690 - 1640 | 1.28 | 0.26 - 0.24 | ? |
| CN triple | 2260 - 2240 | 1.15 | 0.30 - 0.29 | ? |
| C-C | 802 | 1.54 | 0.12 | 0.10 |
| C=C | 1620 | 1.34 | 0.29 | 0.28 |
| N=N | 1630 - 1575 | 1.24 | 0.21 - 0.19 ₅ | ? |
| NN triple | 2360 | 1.09 | 0.26 | 0.24 |
| C-F | 1048 | 1.39 | 0.14 | 0.12 ₅ |
| C-Cl | 732 | 1.78 | 0.34 | 0.32 |
| C-Br | 611 | 1.94 | 0.45 | 0.46 ₅ |
| C-I | 533 | 2.13 | 0.63 | 0.68 |
| N-O | 814 - 751* | 1.37 | 0.07 ₅ - 0.06 | ? |
| N=O | 1681 - 1613* | 1.22 | 0.22 - 0.20 | ? |
| N=O | ca. 1400† | 1.22 | ca. 0.14 | ? |

* In alkyl nitrites.

† In nitrosamines.

Le Fèvre (1959), noting that both ν and b_L^{XY} can vary somewhat with molecular environment so that many fairly similar equations can be written dependently on data sources chosen, suggested the following:

$$\nu = 9273Q - 254.$$

From our viewpoint this is of value since by it the b_L^{XY} 's become predictable of bonds inaccessible to ordinary measurement via the Kerr effect. As illustrations, examples of cases where b_L^{XY} is already known and of others where it has yet to be determined are given in Table 3.

As comment on these it can be said that a b_L^{O-H} of 0.06×10^{-23} is not excluded by the measurements of *n*-alcohols by Le Fèvre, Le Fèvre, Purnachandra Rao, and Williams (1960). The value 0.18×10^{-23} forecast for the C-O bond is quite incorrect; a value for b_L^{C-O} of 0.081 requires ν to be *ca.* 780 cm^{-1} which is much below assignments usually made by infra-red spectroscopists. Malherbe and Bernstein (1952) attribute several frequencies observed in the Raman spectrum of dioxan to ring stretching, and among these is one at 834 cm^{-1} , annotated as polarised and strong; this being used b_L^{C-O} emerges as 0.09. Frequencies near 750 cm^{-1} are recorded for many polymethylene chains, but are commonly ascribed to a rocking mode of the methylene groups; however, Ramsay and Sutherland (1947) consider 802 cm^{-1} to be "probably the symmetrical C-C stretching frequency" in cyclohexane, the compound from which Le Fèvre and Le Fèvre (1955) originally estimated b_L^{C-C} .

It is interesting to examine the reverse use of the equation, whereby a ν_{XY} is estimated from the b_L^{XY} given by the Kerr effect. Table 4 shows this:

TABLE 4

| Bond | b_L^{XY} | ν (cm^{-1}), calc. | ν (cm^{-1}), obs. |
|-----------|------------|--------------------------------------|--------------------------------------|
| C-H | 0.064 | 2950 | 2962 - 2853 |
| C=C | 0.28 | 1605 | 1616 in $\text{CH}_2=\text{CCl}_2^a$ |
| CC triple | 0.35 | 2240 | 2260 - 2100 |
| C=O | 0.23 | 1750 | 1718 in Me_2CO^b |
| C-F | 0.125 | 1000 | 1048 in MeF |
| C-Cl | 0.32 | 710 | 732 in MeCl |
| C-Br | 0.465 | 620 | 611 in MeBr |
| C-I | 0.68 | 556 | 533 in MeI |

^a Corresponding Raman displacement at 1611 cm^{-1} .

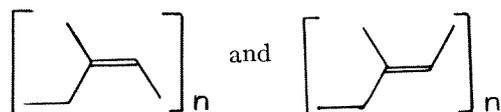
^b 1742 cm^{-1} in vapour.

Agreement appears satisfactory. Carbon monoxide, an isolated bond so to speak, with $r = 1.14 \text{ \AA}$ and $b_L = 0.26$, fits the equation precisely, $\nu(\text{calc.})$ and $\nu(\text{obs.})$ being 2143 cm^{-1} .

Polarisabilities and other Physical Properties

A knowledge of the anisotropy of molecular polarisability can sometimes provide information on the disposition of a given molecule in its crystal lattice. In combination with the measured density of the solid phase, b_1 , b_2 , and b_3 yield three "molecular refractions", R_1 , R_2 , and R_3 , from which three corresponding refractive indexes can be extracted. If one of these equals one of those observed for the crystal, the "lie" of one of the molecular axes is determined. Examples of this type of use are seen in Le Fèvre and Le Fèvre's (1955) treatment of naphthalene, or that by Bunn and Daubeny (1954) of hexatriacontane.

A number of other physical measurements in which either molecular or bond polarisabilities appear to be important are also receiving attention; two will be mentioned but cannot now be enlarged upon. The first concerns molar Verdet constants. In their 1955 Review the Le Fèvre's mentioned that these, for many molecules, seem to be linearly related to the sums of the products of the various principal molecular polarisabilities, *viz.* $b_1b_2 + b_2b_3 + b_3b_1$. The second concerns stress birefringence, especially in polymers. If a macromolecule is made up of mers [sic], each with polarisabilities b_x , b_y , and b_z in random array, then the birefringence Δn induced by a stress on the material in bulk is given by the "stress optical coefficient" $C = 2 \pi(n^2 + 2)^2 (b_x - b_y) / 45nkT$, where n is the ordinary refractive index. As stated above, both rubber and gutta-percha are being studied by us; these are poly-*cis*- and poly-*trans*-isoprenes respectively, and the constituent mers [sic] are



From our C-C, and C=C bond data, $b_x - b_y$ is *ca.* 0.25×10^{-23} for both. With $n = 1.52$ the calculated stress optical coefficient emerges at $2.1 - 2.2 \times 10^{-10}$ cm²/dyne, which agrees with the value listed by Stein (1956) for Hevea Rubber at 30°. We are hoping that similarly satisfactory calculations will apply to other polymers now engaging Dr. Sundaram.

Possible Future Developments

By Liversidge's Will the lecturer is charged also with "drawing attention to the research work which should be undertaken". Where the wider aspects of my subject are concerned, perhaps this can most neatly be done by saying that nine ways may be foreseen whereby the imposition of electric or magnetic fields may cause anisotropy of a liquid or gas composed of anisotropic molecules, whose random orientations are partially destroyed by orientations caused by the applied field. In theory, effects should be observable on the dielectric constant ϵ , the magnetic permeability μ^* , and the refractive index n :

| <i>Field Applied</i> | n | ϵ | μ^* |
|----------------------|------------|-------------------|---------|
| Electric | Δn | $\Delta \epsilon$ | ? |
| Magnetic | Δn | ? | ? |
| Optical | ? | ? | ? |

Of the six possible phenomena associated with electric and magnetic fields, three have been discovered by experiment, and only one of these - the Kerr effect - can be said to have

been extensively investigated from a molecular structural viewpoint. Even so, much straightforward work remains to be done, e.g., the dependence of the Kerr effect on state - a matter taken up so far only in two papers, and which really requires a long series of patient measurements on gaseous dielectrics.

We in Sydney are beginning a study of "magnetic birefringence" - the "Cotton-Mouton effect" (in which the molecular anisotropies of both optical polarisability and magnetic susceptibility are concerned); our plans are to proceed along lines parallel to those used with the Kerr effect. The other "effects" - less interpretable and more difficult to detect - we leave to resourceful posterity!

The idea that a very intense beam of polarised light ("optical fields") may cause anisotropy of observable properties is due to Dr. A.D. Buckingham, an old student and one-time collaborator of ours. His theory is set out in papers in 1956 and 1957. Luminous fluxes of a very high order will be required if his "effects" are to be amenable to laboratory study; perhaps the techniques of flash photolysis will help - anyway, here is a discovery half made!

Acknowledgements

I desire to record my deep gratitude to all my co-workers and students, past and present, who have contributed magnificently by their labours, and taught me so much by their discussions. Their names have been mentioned above and occur again in the references listed below. Especially do I acknowledge my debt to my wife, Dr. Catherine LeFèvre, my equal collaborator for nearly 30 years, without whose persistent struggles with the principles and techniques of physical optics, never-ending patient experimentation, and help in innumerable ways, this work could never have been done in the University of Sydney.

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*Sources not listed here may be found in the 1955 review by Le Fèvre and Le Fèvre.