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The Faraday Effect in Transparent Regions—An Unusual Method for the Investigation of Molecular Structures

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I. INTRODUCTION

Although 125 years have elapsed since the discovery by Faraday[1] in 1845 of the phenomenon of the rotation of the plane of polarisation in a magnetic field and although numerous investigators both in France and abroad devoted their lives to a profound study of this phenomenon and its applications in structural chemistry, in 1970 the Faraday effect is quite unfamiliar to chemists as a research technique.

The literature, which includes more than 200 papers, clearly shows that a powerful technique now exists whereby it is possible to solve, sometimes very successfully, a large number of problems in structural chemistry. Numerous meetings with investigators from different countries at conferences have revealed a considerable interest in this method. The question thus arises why the Faraday effect is known only to a limited circle of specialists while NMR, infrared, and ultraviolet spectroscopic techniques have become common and classical procedures. The answer is probably that all the papers describing the principles of the method and its applications have been published in French and, with rare exceptions, in French periodicals. It is therefore an urgent necessity to overcome the language barrier in order that the Faraday effect may become internationally known. Our attempt to solve this difficult problem was stimulated by the invaluable support of many well known investigators such as C. A. Coulson, H. D. Ballhausen, C. K. Jorgensen, A. Julg, R. Daudel, A. Sladkov, and J. R. van Wazer, to whom we are indebted for their assistance and advice in the compilation of this review.

II. WHAT IS THE FARADAY EFFECT?

As early as 1845, Faraday[1] made the following fundamental discovery: any transparent substance placed in a magnetic field H rotates the plane of polarisation when monochromatic light is passed through it. This phenomenon may be called magnetic rotation by analogy with natural rotation, although molecular asymmetry is evidently important for the latter, while the former is shown by any substance in a magnetic field. Faraday's experiments were repeated and extended by Becquerel[2], Mathiessen[3], and especially Verdet[4], who was the first to find a quantitative expression for the effect in the form

$$\alpha = \rho \int_0^l H dl,$$

where l is the optical pathlength in the test substance and ρ a characteristic constant for the substance, which has been called the Verdet constant. Thus measurement of the angle α permits in principle the determination of the Verdet constants of the relevant compounds and also the corresponding molecular magnetic rotation $(\rho)_M$, defined by the expression

$$(\rho)_M = \frac{\rho}{d} \cdot M,$$

where M and d are the molecular weight and specific gravity of the substance.

This in broad outline is the observed phenomenon and about a century elapsed since its discovery before the following two fundamental questions were formulated:

1. What is the reason for the rotation of the plane of polarisation?
2. Is the Verdet's formula rigorously valid?

The answer to the first question in terms of classical quantum mechanics has been given in publications which are virtually inaccessible to physical chemists without sufficient experience in quantum-chemical calculations. Indeed the theoretical aspect of the magnetic rotation of the plane of polarisation (the electromagnetic wave, the magnetic field, and the set of molecular orbitals in the strong interaction condition) is so complex that, listening to lectures by theoretical physicists developing the formal mathematical side of the problem, one might sometimes ask whether the effect under discussion is indeed the one first observed by Faraday. To see this, it is sufficient to read only a few pages in papers by Kronig[5], Rozenfeld[6], Kramers[7], Groenewege[8], Smet[9-11], or I'Haya[12]. The concept which we shall now develop in a few words will undoubtedly arouse protests by theoreticians but it has the

advantage of a simple description of the basis of the phenomenon.

The presence of a magnetic field leads to complete loss of symmetry by molecular orbitals. If Ψ_0 denotes the wave function in the absence of the field, the perturbed wave function is

$$\psi = \psi_0 + \sum_k c_k \psi_k ,$$

where Ψ_k are the wave functions of the excited molecular states.

The change of Ψ_0 under the influence of the field H appears to involve the mixing of the ground and excited molecular states. It has been shown[13] that in first-order perturbation theory

$$c_k = \frac{-aH \int \psi_0 \frac{\partial}{\partial \theta} \psi_k d\tau}{E_0 - E_k} ,$$

where θ is the polar angle reckoned from the direction of H and E_0 and E_k are the energies of the levels corresponding to Ψ_0 and Ψ_k. It is immediately clear that the contribution by Ψ_k to perturbation will be non-zero only when Ψ_k includes symmetry elements antisymmetric to Ψ_0. This is in fact why, when Ψ_0 is the $2p_z$ orbital, only the $3d_{xy}$ orbital makes an appreciable contribution to the deformation of Ψ_0 and, when Ψ_0 is an s orbital, no orbital with an energy lower than that of the $4f$ orbital can be involved in the perturbation. As a result, one may say *a priori* that the Faraday effect due to the π electrons in the molecule is much greater than that due to the σ electrons, since $E_{2p_z} - E_{3d_{xy}}$ is always much smaller than $E_s - E_{4f}$. Subsequently we shall see that this is in fact so. Thus in a magnetic field molecular orbitals completely lose their symmetry and this is the reason for the optical anisotropy and the further consequences are fully analogous to those in the natural rotation of the plane of polarisation[14].

The second question posed above is no less important: one can show that the rotation α is not in fact strictly proportional to H but is expressed by a limited series

$$\alpha = aH + bH^2 + cH^3 + \ldots$$

Usually the "double rotation 2α", i.e. the sum of the rotations $+\alpha$ and $-\alpha$ observed for two opposite values of the field $+H$ and $-H$ is measured experimentally. This procedure eliminates terms proportional to the even powers of H in the expression for α. Therefore, if cH^3 is negligibly small, then $\alpha \propto H$, in agreement with Verdet. Detailed calculation of the quantities a and c shows that this is true, provided that H does not exceed 2.5×10^4 gauss. This limits has not so far been attained in classical apparatus for the measurement of the Faraday effect in the transparency range; the most powerful of these, which we have in our laboratory, has $H_{max} = 1.5 \times 10^4$ gauss. However, one must recognise that an increase of H_{max}, which might nowadays be expected by specialists in the field of the Faraday effect, would face the boldest investigators with the difficulties of non-linear quantum electrodynamics; their results could not be compared directly with the data of their colleagues, who, unable to use the new facilities for practical reasons, would continue to work in the region where α is fairly exactly proportional to H. This is indeed the case, but, having made these philosophical remarks, we shall now turn to the actual experimental technique and the results which it can yield.

III. EXPERIMENTAL ARRANGEMENT AND ACCURACY OF MEASUREMENTS

The optical system consists of a mercury lamp S emitting a characteristic spectrum from which the required line may be isolated by a monochromator M of TREGOR type. The monochromatic light beam passes through a polariser P and then through a polarimetric cuvette C in the gap of the electromagnet (Fig. 1). The rotation of the plane of polarisation is read off to within 0.01° with the aid of a Lippich polarimeter. The electromagnet is supplied with currents up to 200 A stabilised to within 1%, from a 150 V supply. The maximum magnetic field strength in the centre of the gap is of the order of 1.5×10^4 gauss for a homogeneity of 10^{-5} gauss cm^{-1} and a gap of 7 cm wide. The polarimetric cuvette, with an average length of 3 cm and a working volume of 2 cm^3, is thermostatted and located in the gap by means of adjustable brass holders clamped to the yoke of the electromagnet.

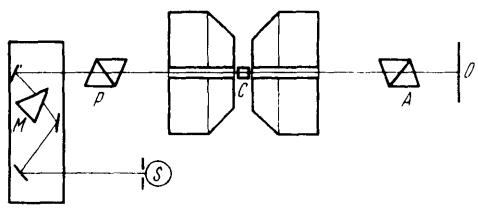


Figure 1.

The polarimetric readings can be made with two opposite directions of H and the resulting "double rotations 2α" reach on average 75°. To obviate the necessity for an accurate determination of the magnetic field gradient along the cuvette, relative measurements are usually made. If we denote by subscripts e and i the standard and test substances respectively, then

$$\frac{\alpha_i}{\alpha_e} = \frac{\rho_i}{\rho_e}$$

or, introducing the specific rotatory power (ρ_i) and the molecular rotatory power $(\rho_i)_M$:

$$(\rho_i)_M = \frac{\rho_e}{\alpha_e} \alpha_i \frac{M_i}{d_i} ,$$

where M and d denote the molecular weight and the specific gravity of the test substance. Doubly distilled water is used as a classical reference standard, since its Verdet constant at 20°C and a wavelength of 546 nm (the green line in the discharge spectrum of mercury) has been measured with a high accuracy by de Mallemann et al.[15] as 4.482 μrad (microradians). It was established that the magnetic rotation of the substance depends on the wavelength at which the measurements are made[16], on temperature[17,18], and on the physical state of the test substance[19]. As regards the first factor, it is assumed that the substance exhibits *normal dispersion*, provided that the measured Verdet constants at $\lambda_1 = 578$ nm, $\lambda_2 = 546$ nm, and $\lambda_3 = 436$ nm satisfy the relations

$$\frac{\rho(\lambda_3)}{\rho(\lambda_1)} = 1.86 \text{ and } \frac{\rho(\lambda_2)}{\rho(\lambda_1)} = 1.13 .$$

The dispersion for covalent and diamagnetic molecules and molecules without transition elements is always normal as long as the first vertical transition for these compounds in the ultraviolet region lies below 280 nm.

The effect of temperature and the physical state on the magnetic rotation of a given substance has been the subject of numerous investigations. In particular, de Mallemann established that

$$(\Omega)_M = \frac{9n}{(n^2+2)^2}(v)_M$$

is an invariant quantity for all changes [in the system]. In this formula n is the refractive index at the experimental wavelength and temperature[19]. Recently Dagnac-Amans[20] showed that molecular magnetic rotation can always be used over a wide temperature range centres on 20°C for a satisfactory description of the magneto-optical properties of a single molecule. She also succeeded in showing, having confirmed the individual results of the work of Dupouy and Fert[17], that magnetic rotation decreases slightly (and linearly) with increasing temperature (except for H_2O and D_2O). Table 1 lists specific data confirming this finding.

Table 1.

CS_2	$y=-0.658\ t+781.6$	$CH_3(CH_2)_2CH_2OH$	$y=-0.024\ t+342.0$
C_6H_6	$y=-0.216\ t+841.8$	CH_3COCH_3	$y=-0.024\ t+249.3$
CCl_4	$y=-0.073\ t+472.0$	CH_3OCH_3	$y=-0.020\ t+191.7$
$CH_3CH_2CH_3$	$y=-0.071\ t+258.0$	D_2O	$y=+0.012\ t+77.8$
SO_2	$y=-0.066\ t+219.5$	H_2O	$y=+0.006\ t+71.6$

On our apparatus, it is possible to investigate either liquids in the temperature range between −120° and +120°C or solutions of sparingly soluble substances in a suitable solvent. The optical measurements do not present any difficulties in the first case and one can be certain that the accuracy attained in the measurement of molecular rotation is about 0.3%. In the second case fundamental difficulties arise because of the importance of the choice of solvent. Initially one must make sure that in the test solution there are no chemical or physical interactions between the solute and solvent and that one may employ the relations established by Verdet[4] for ideal mixtures, according to which each component makes an additive contribution to the overall magnetic rotation. Then it is necessary to select a solvent whose Verdet constant differs sufficiently from the analogous constant of the test solution. This factor, which is very sensitive in practice, must be satisfied with great precision, since it determines the success of the measurements. In view of all these considerations, measurements in solutions must be resorted to only in extreme cases and the accuracy of the molecular rotation thus obtained does not exceed 1%. In an attempt to obviate this difficulty, Zarzycki and Naudin[21] devised a special apparatus permitting observations on compounds in the liquid state, whose melting points may reach 1100°C.

After this brief description of the classical experimental arrangement, we proceed to the review of the fundamental applications of the method in studies on problems in structural chemistry, which are of the most immediate interest.

IV. THE FARADAY EFFECT AND THE ADDITIVE PROPERTIES OF MATTER

We have just seen how magnetic molecular rotation (a generalised property) characterising the test substance may be determined by a simple polarimetric measurement, provided that the specific gravity is known. Because of this generality, non-specialists believed for a long time that the Faraday effect constitutes a less powerful method than NMR or infrared spectroscopy, since the latter make it possible, in principle, to determine the essential characteristics of the nucleus or a given bond. We shall now see that in fact such discrimination is invalid and is based solely on the ignorance of the magneto-optical phenomenon. Magnetic rotation of polarisation is an additive property of matter: the question arises of the significance of this assertion and its basis. All the experimental data accumulated during the period since the Faraday effect has been known indicate a systematic additivity of magnetic rotation, similar to that discovered by Pascal and coworkers[22] in diamagnetism, which frequently makes it possible to calculate with surprising accuracy the molecular rotation of a compound, provided that two conditions are satisfied: (1) only covalent, normal, diamagnetic, σ, or π localised bonds are present; (2) the bond constant has been explicitly defined.

In 1960 Gallais and Voigt[23] first suggested that additivity may be expected for magnetic rotation per bond. The difficulty of determining the magnetic rotation parameters referred to individual bonds consists in the necessity of separating a generalised quantity for the atom into components characterising individual bonds in such a way that each bond constant is independent of the individual characteristics of the others. Moreover, the quantity characteristic of the atom as a whole must evidently be the same every time. This problem hardly exists in organic chemistry, since carbon almost always exhibits the same coordination and employs four valence electrons. However, it is important for inorganic chemistry, where atoms can have significantly different coordinations. In order to overcome this difficulty, it is necessary (1) to define bond constants in such a way that they are independent of the coordination of the atoms involved in the given bond and (2) account must be taken of the behaviour of lone electron pairs not involved in any interatomic bond.

The first conditions may be satisfied simply by dividing the generalised quantity characterising the atom into equal parts among the n_E valence electrons, assuming that they are all equally active as regards the optical, magnetic, and magneto-optical properties. The modulus α (for refraction, magnetisation, and magnetic rotation) of a single σ or π bond between two atoms A and B is then uniformly represented by the symbol

$$\alpha\left(\frac{A}{n_A}-\frac{B}{n_B}\right)$$

and if the atom X contributes two electrons to the bond (a double bond, or a donor–acceptor bond in which X is an electron-donating atom), its contribution to a bond of this kind becomes $2X/n_X$, etc.

Tables 2–4 present data on the magnetic rotation due to the commonest bonds, determined in accordance with the above principles from chemical data for carbon[23,24], boron[25-30], aluminium[31,32], gallium[33], nitrogen[23,34], sulphur[20,35], and phosphorus[36,37]. Having at one's disposal the required set of bond constants, it is easy to calculate the magnetic rotation, provided that, taking into account Eqn. (2), the contribution $\alpha(e)$ by lone electron

Table 2.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\sigma}$	18.50	$\left(\frac{C}{4}-\frac{N}{3}\right)$: (NR_3)	47.0
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\pi}$: $(H_2C=CH_2)$	117	$\left(\frac{3C}{4}\equiv\frac{N}{1}\right)_{\sigma+\pi}$: nitriles	65.5
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\pi}$: $(HC\equiv CH)$	77.5	$\left(\frac{C}{1}\equiv\frac{2N}{3}\right)_{\sigma+\pi}$: isonitriles	119
$\left(\frac{C}{2}=\frac{C}{2}\right)_{\sigma+\pi}$	135	$\left(\frac{C}{4}-\frac{Si}{4}\right)$	74
$\left(\frac{3C}{4}\equiv\frac{3C}{4}\right)_{\sigma+\pi}$	173	$\left(\frac{C}{4}-\frac{Ge}{4}\right)$	101
$\left(\frac{C}{4}-H\right)$	27.25	$\left(\frac{C}{4}-\frac{Sn}{4}\right)$	174
$\left(\frac{C}{4}-F\right)$	20	$\left(\frac{C}{4}-\frac{Pb}{4}\right)$	278
$\left(\frac{C}{4}-Cl\right)$	131	$\left(\frac{C}{4}-\frac{Be}{2}\right)$	190
$\left(\frac{C}{4}-Br\right)$	267	$\left(\frac{C}{4}-\frac{Hg}{2}\right)$	260
$\left(\frac{C}{4}-I\right)$	566	$\left(\frac{Si}{4}-\frac{O}{2}\right)$: $(Si(OR)_4)$	28.9
$\left(\frac{C}{4}-\frac{O}{2}\right)$	14.2	$\left(\frac{Si}{4}-Cl\right)$: $(SiCl_4)$	171
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: acid	30.6	$\left(\frac{Si}{4}-\frac{Si}{4}\right)$: (Si_2R_6)	325
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: aldehydes	35.5	$\left(\frac{N}{3}-H\right)$: (R_2NH)	20
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: ketones	41.7	$\left(\frac{O}{2}-H\right)$: $(R\cdot OH;\ R\cdot CO_2H)$	28.0
$\left(\frac{C}{4}-\frac{S}{2}\right)$	126	$\left(\frac{S}{2}-H\right)$: (RSH)	158
$\left(\frac{C}{2}=\frac{S}{1}\right)_{\sigma+\pi}$: (CS_2)	385		

Table 3.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{B}{3}-\frac{C}{4}\right)$	45	$\left(\frac{B}{3}-H\right)$	—
$\left(\frac{B}{3}-\frac{O}{2}\right)$	18	$\left(\frac{B}{3}-\frac{B}{3}\right)$	51
$\left(\frac{B}{3}-\frac{S}{2}\right)$	140	$\left(\frac{Al}{3}-\frac{C}{4}\right)$	138
$\left(\frac{B}{3}-\frac{Cl}{1}\right)$	145	$\left(\frac{Ga}{3}-\frac{C}{4}\right)$	165
$\left(\frac{B}{3}-\frac{Br}{1}\right)$	300	$\left(\frac{In}{3}-\frac{C}{4}\right)$	307

pairs is added. This condition is so important that its neglect immediately leads to considerable errors: unfortunately, in most studies on molecular interaction and almost always in the field of dipole moments, the contribution by lone electron pairs of atoms in the molecule is disregarded in the calculation of molecular quantities. Soon we shall see that the magnetic rotation which may be attributed to lone electron pairs is usually very considerable. There exists a simple method of estimating their contribution to a first approximation: it was used for the first time in the field of molecular refraction by Le Fevre and coworkers[38] at the time when we were preparing to publish analogous reports on the Faraday effect[39]. For this purpose, one must consider the changes in the magnetic rotation $\rho(C-E)$ due to the carbon–element bond as a function of the position of E in the Periodic System.

Table 4.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{P}{3}-\frac{C}{4}\right)$	159	$\left(\frac{S}{2}-\frac{C}{4}\right)$	126
$\left(\frac{P}{3}-\frac{O}{2}\right)$	110	$\left(\frac{S}{2}-\frac{O}{2}\right)$	105
$\left(\frac{P}{3}-\frac{S}{2}\right)$	364	$\left(\frac{S}{2}-\frac{Cl}{1}\right)$	286
$\left(\frac{P}{3}-\frac{Cl}{1}\right)$	262	$\left(\frac{S}{2}-H\right)$	158
$\left(\frac{P}{3}-\frac{Br}{1}\right)$	550	$\left(\frac{S}{2}-\frac{S}{2}\right)$ (RS—SR)	319
$\left(\frac{P}{3}-\frac{P}{3}\right)$ (R_2P-PR_2)	349	$\left(\frac{Se}{2}-\frac{C}{4}\right)$	200
$\left(\frac{As}{3}-\frac{C}{4}\right)$	190	$\left(\frac{Se}{2}-H\right)$	250
$\left(\frac{As}{3}-\frac{O}{2}\right)$	150		

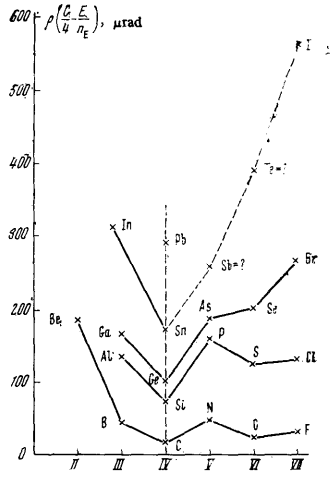


Figure 2.

Fig. 2 shows that the rotation increases rapidly within each Group, whereas in each horizontal Period it passes through a minimum when E belongs to Group IV. A detailed study of these changes leads to progress in the solution of the problem, which consists in the separation of the effects of various factors on the magnetic rotation due to the bond. Four factors may be regarded *a priori* as important: (1) the change in the overall value for the atom E involved in the bond $(C/4-E/n_E)$, while the analogous quantity for carbon remains constant; (2) proportionality to the amount

of ionic character of the bond; (3) the type of hybridisation of the atom E; (4) and, evidently, the activity of the corresponding lone electron pair of the atom E.

Simple considerations demonstrate that the third and fourth factors are dominant in the variation of $\rho(C-E)$. On the other hand, the decrease of the magnetic rotation due to the bond, on passing from Group II to IV, may be attributed only to the first and second factors and the minimum in the observations when E belongs to Group IV must be caused by the simultaneous operation of the first and second factors, the second predominating. Analysis of the left-hand part of the plot in Fig. 2 shows how $\rho(C-E)$ changes as a function of the hybridisation of the atom E. On passing from Group II to Groups III and IV, the fraction of s character of the atomic orbitals involved in the bond increases from 50 to 75 (in accordance with the change in hybridisation: $sp-sp^2-sp^3$). One must assume that the s character of the atomic orbitals of E and the rotation due to the (C−E) bond vary in parallel. Thus we arrive at the hypothesis, put forward by Le Fevre and coworkers[38] and Gillis[40] to account for the decrease of the (C−E) bond refraction in the given case. However, contrary to the postulates of these investigators, there is no doubt that the fraction of s character of the bond and refraction or rotation are not linearly related. Admittedly, in any type of linear relation between $\rho(C-E)$ and the amount of s character there should be no change in $\rho(C-E)$ on passing to Groups V, VI, and VII, since the hybridisation of nitrogen atoms in NH_3, of oxygen atoms in OR_2, and of fluorine atoms in FR remains close to sp^3. The increase of $\rho(C-E)$ actually observed appears to be caused, under these conditions, by the contribution from the lone electron pairs of the atom E, which may be calculated using the definition of bond rotation and the symbolism of the systematic additive scheme. Thus for phosphorus (a Group V element), we have

$$\rho\left(\frac{C}{4}-\frac{P}{3}\right)=\rho\left(\frac{C}{4}-\frac{P}{5}\right)+\frac{1}{3}\rho(d_P)=\rho^*(C-P)+\frac{1}{3}\rho(d_P),$$

and by hypothesis

$$\rho^*(C-P)=\rho\left(\frac{C}{4}-\frac{Si}{4}\right),$$

whence

$$\rho(d_P)\sim 3\left[\rho\left(\frac{C}{4}-\frac{P}{3}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]\sim 225\ \mu\text{rad}.$$

Similarly, for a Group VI element,

$$\rho\left(\frac{C}{4}-\frac{S}{2}\right)=\rho\left(\frac{C}{4}-\frac{S}{6}\right)+\frac{1}{2}\rho(2d_S)=\rho^*(C-S)+\rho(d_S);$$

using

$$\rho^*(C-S)=\rho\left(\frac{C}{4}-\frac{Si}{4}\right);$$

we have

$$\rho(d_S)=\left[\rho\left(\frac{C}{4}-\frac{S}{2}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]\simeq 52\ \mu\text{rad},$$

and, finally, for a Group VII element, for example chlorine, we have

$$\rho\left(\frac{C}{4}-\frac{Cl}{1}\right)=\left[\rho\left(\frac{C}{4}-\frac{Cl}{7}\right)+\rho(3d_{Cl})\right]=\rho^*(C-Cl)+3\rho(d_{Cl}),$$

$$\rho(d_{Cl})=\frac{1}{3}\left[\rho\left(\frac{C}{4}-\frac{Cl}{1}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]=19\ \mu\text{rad}.$$

The contributions by the lone electron pairs calculated in this way are listed in Table 5. Evidently the magnetic rotation due to a lone electron pair is often very considerable (compared with the contribution by the bond electron pair) and is a maximum for Group V elements. This result is consistent with the well known fact that phosphorus is a more powerful electron donor than sulphur and SX_2 molecules are stronger Lewis bases than XCl. The previous conclusions are based to a significant extent on the occurrence of a systematic additivity (which has not yet been discussed) of the magnetic rotation due to bonds, provided that the latter are covalent, normal, diamagnetic, and localised. The experimental evidence for such systematic behaviour has quite recently received valuable theoretical support in a paper by Daudel, employing analysis based on the "cell" theory† [41-44]. Systematic additivity is confirmed with the aid of the cell concept provided that three criteria are satisfied[45].

1. There is a clear subdivision of molecular space into cells (the probability of the residence of a single electron within a specified sphere is close to unity).

2. The quantity A is the sum of the A_i which are in turn expressed thus:

$$A_i=\int_{E-L_i} dv_{p+1}\ \ldots\ dv_n \int_{L_i}\psi^* A_{op}\psi dv_1\ \ldots\ dv_p,$$

and $A=\Sigma A_i$ (it is assumed that the cell L_i contains p electrons).

Table 5.

Element	Group V	Group VI	Group VII
Element E	N	O	F
$\rho(D)_E$, μrad	86	(−4.3)	(+0.5)
Element E	P	S	Cl
$\rho(D)_E$, μrad	255	52	19
Element E	As	Se	Br
$\rho(D)_E$, μrad	267	103	55
Element E	—	—	I
$\rho(D)_E$, μrad	—	—	131

3. The values of A_i for a given type of cell vary little in the series of molecules investigated.

Criterion *2* is fundamental to the interpretation of Daudel et al.[45], who were able to show that magnetic rotation satisfies it and therefore the classification of the additive properties in the Faraday effect is justified[46,47].

Since this is so, subsequent solution of problems in structural chemistry on the following basis is permissible: *all structural features of compounds with covalent, diamagnetic, and localised σ and π bonds must be duly reflected to some degree in a deviation from the law of additivity*. However, before concluding the section of definitions, we feel it desirable to consider the deeper significance of the systematic scheme. Such a scheme is very useful to the experimenter, who can ascertain by simple addition the purity of a compound just obtained. However, in terms of ideas, one must be firmly convinced that the bond constant is a constant quantity regardless of the environment of the bond in the remaining part of the molecule. This is undoubtedly shocking to critical minds.

† See Daudel's book[185] (Editor) [the original French term is "loge" (Ed. of Translation)].

How is it possible for magnetic bond rotation to be invariant in a molecule, while all other properties (vibration frequencies, bond lengths, ionic character, etc.) change? This remark in fact led us in 1964 to make a closer examination of the implications of the systematic scheme.

We know that the magnetic polarisability of a σ bond depends primarily on the shape of its electron cloud. We believe that the simplest semiempirical parameter providing a description of this configuration should be the partial ionic character of the bond as defined by Pauling. If we wish to find a relation between the rotation p_{AB} of a covalent σ bond (A–B) and the amount of its ionic character I_{AB}, it is necessary to have at ones disposal a method for calculating the effective value of I_{AB} for various possible situations in the molecule. Ultimately we decided on an iterative method[48] based on the use of self-consistent Pauling exponential functions modified and extended to the molecules M(XYZ...). A formal description of this procedure was given by Daudel in 1946 for symmetrical molecules MX_n.[49] In this way we were able to compare the effective values of I_{AB} obtained for all bonds in any covalent compound with the experimental values of ρ_{AB} obtained for these series of compounds without needing to postulate the constancy of the modulus of bond rotation, which is now regarded as a function of I_{AB}.

Table 6.

Compound	I_{BC}	ρ_{BC}	I_{BCl}	ρ_{BCl}
BCl_3	—	—	12.2	143.4
BCl_2R	3.9	57.9	13.1	140.7
$BClR_2$	4.6	50.4	14.4	136.8
BR_3	5.1	45.0	—	—

This enabled us to demonstrate a linear relation between ρ_{AB} and I_{AB}, which is demonstrated in Table 6 for certain most common bonds of boron[50] and phosphorus[51]. We chose these examples from others, since subsequently the corresponding equations will prove useful. Examination of Table 6 shows in the first place that b_{AB} is in all cases negative: it is quite logical that a higher value of I_{AB} is associated with a greater shift of the electron cloud and its concentration at the more electronegative atom. On the other hand, its deformability under the influence of the magnetic field is weaker and consequently the Faraday effect associated with this bond is smaller. The numerical value of b_{AB} is equally interesting. For similar bonds of boron and phosphorus (B–C and P–C, B–O and P–O), the b_{AB} values are virtually identical, which must be attributed to the similarity of the electronegativities (1.9 and 2.1 on Gordy's scale[52]). We may note further that b_{AB} decreases and tends to zero when the difference between the electronegativities δ_X of the atoms A and B increases. The limit is virtually attained for the (B–O) and (P–O) bonds ($\delta_X = 1.5$), which suggests that any (A–B) bond with $\delta_X \geqslant 1.5$ will have $b_{AB} = 0$ and will therefore give rise to a constant magnetic rotation regardless of the molecule in which this bond is located. In particular, the (P–F) bond is of this type, provided of course it is a σ bond. As this is correct, there arises immediately the following valid question concerning all that has been said above: how to reconcile the experimental finding of a systematic additivity of the moduli (constants) and the existence, proved theoretically, of a linear variation of these constants as a function of I. It is simplest to analyse one example, which provides a perfectly clear illustration: Table 6 shows how the ionic character of the (B–C) and (B–Cl) bonds varies in the $BR_{3-x}Cl_x$ series; evidently in the mixed compound $BRCl_2$, I_{BC} and I_{BCl} are respectively smaller and bigger than the corresponding quantities in BR_3 and BCl_3. Since b_{BC} and b_{BCl} are negative, ρ(B–C) and ρ(B–Cl) will be respectively bigger and smaller than the values in BR_3 and BCl_3. Thus it is sufficient to show numerically, which is not difficult, that the two deviations cancel out, since the essential features of the systematic additivity with constant moduli again become evident (Table 7).

Table 7.

Bond	$e_{ij} = a_{ij} + b_{ij} I_{ij}$	Bond	$e_{ij} = a_{ij} + b_{il} I_{ij}$
B–O	$\rho = 32.6 - 0.7 \cdot I_{BO}$	P–O	$\rho = 110 - 0 \cdot I_{P-O}$
B–Cl	$\rho = 180 - 3 \cdot I_{BCl}$	P–Cl	$\rho = 294 - 3.3 \cdot I_{PCl}$
B–C	$\rho = 99.6 - 10.7 \cdot I_{BC}$	P–C	$\rho = 182.9 - 9.2 \cdot I_{PC}$

The systematic additivity is in fact due to the cancellation of the terms $b_{BA}I_{AB}$ within the molecule. Thus everything falls into place. We believe that this result is doubly valuable. Firstly, it shows that the existence of systematic additivity is not fortuitous and, in addition, it provides a simple interpretation of the existence of certain σ covalent molecules which do not obey systematic additivity no matter which property one attempts to treat as an additive function. We preferred not to discuss this in Section II, in order not to draw readers' attention to details, which might have made it difficult to assimilate the main ideas. However, the time has now come to deal with this question: it concerns essentially molecules of the type $CCl_{4-x}H_x$. As early as 1910, Pascal[53] noted their anomalous diamagnetic behaviour, while Gallais and Voigt somewhat later[23] arrived at a similar conclusion concerning the Faraday effect.

Evidently, there should be no intramolecular compensation in these molecules. This compensation occurs only if the electronegativity of the central atom M is outside the range of electronegativities of the substituents X and Y (and b_{MX} and b_{MY} are negative). Halogenomethanes do not exhibit additivity, since this condition does not hold for them and indeed

x_H	x_C	x_{Cl}
2.10	2.55	2.97

The observations which have worried the specialists in the field of the additive properties of matter for many years can be explained similarly[50]. The additivity of the Faraday effect was discussed and demonstrated in such detail in order to employ the deviations from this law for the solution of specific problems in structural chemistry.

V. MAGNETO-OPTICAL INVESTIGATION OF CONJUGATION PHENOMENA

In 1960 we made a detailed study of additive properties in the presence of electrons delocalisation in the molecule. Our investigation concerned primarily conjugated aliphatic

systems (pure hydrocarbons). The results are presented in Table 8; we established that the presence of a delocalised π-electron system in open-chain molecules always leads to a considerable positive deviation from additivity[54]. This fundamental result implies that the experimental molecular rotation (A) of a conjugated compound is always higher than the theoretical value (B) which may be calculated by additivity on the assumption that the molecule contains only localised bonds. Thus the exaltation of magnetic rotation (E) due to conjugation (briefly, conjugation exaltation) proves in addition to be constant for a given conjugation fragment and, conversely, is appreciably different for different conjugation fragments (Table 8). Analogous results were obtained for a large number of conjugated aliphatic moieties incorporating (C=O) and (C=N) bonds[55-58].

Table 8.

Formula	A	B	E
$CH_3=CH-CH=CH_2$	570	453	+117
$CH_2=CH-CH=CH-CH_3$	632	514	+118
$CH_2=CH-CH=CH-C_2H_5$	716	599	+117
$CH_3-CH=CH-CH=CH-CH_3$	695	575	+120
$CH_3-CH=CH-CH=CH-C_2H_5$	779	660	+119
$CH_3-CH=CH-CH=CH-C_3H_7$	853	733	+120
Mean			+119
$CH_2=C(CH_3)-CH=CH_2$	632	514	+118
$CH_2=C(CH_3)-C(CH_3)=CH_2$	695	575	+120
$CH_3-CH=C(CH_3)-CH=CH_2$	705	576	+129
$(CH_3)_2C=CH-CH=CH_2$	700	576	+124
$(CH_3)_2C=CH-CH=CH-CH_3$	762	637	+125
Overall mean (from No.1 to 11)			+121
$CH_3-CH=C(CH_3)-C\equiv CH$	633	560	+73
$CH_3-CH=C(CH_3)-C\equiv C-CHOH-C_3H_7$	919	867	+52
$C_4H_9-C\equiv C-C(CH_3)=CH-CH_3$	916	852	+64
Mean			~+63
$C_2H_5-C\equiv C-C\equiv CH$	641	566	+75
$C_4H_9-C\equiv C-C\equiv CH$	791	712	+79
$C_2H_5-C\equiv C-C\equiv C-COH(CH_3)_2$	898	823	+75
$C_4H_9-C\equiv C-C\equiv C-COH(CH_3)_2$	1047	969	+78
Mean			+77
$C_4H_9-C\equiv C-C\equiv C-C(CH_3)=CH_2$	1080	982	+ 98
$CH_2=CH-CH=CH-C\equiv CH$	786	645	+141
$CH_2=CH-CH=CH-CH=CH_2$	873	662	+211
$C_3H_7-CH=C=CH_2$	572	560	+ 12
$C_4H_9-CH=C=CH_2$	643	633	+ 10
$C_6H_{13}-CH=C=CH_2$	791	779	+ 12
$CH_2=CH-CH=C=CH_2$	664	549	+115
$C_2H_5-CHOH-CH=C=CH-CH=CH-CH_3$	965	844	+121
$C_2H_5-COH(CH_3)-CH=C=CH-CH=CH_2$	985	872	+113
$CH_3-COH(CH_3)-CH=C=CH-CH=CH_2$	935	806	+129
Overall mean (from No.25 to 28)			+120

Since the existence of E is associated with the delocalisation of π electrons, it was logical to find if E depends in some simple manner on the parameters employed in theoretical chemistry to describe delocalisation. For this purpose, we calculated in terms of the Hückel approximation the π-electronic structures of all the molecules investigated. We obtained the bond indices p_{rs}, the charges q_r localised at the atoms, and the free valence indices I_r,[59-61] and concluded that the sum of the free valence indices is in fact the required parameter, since the E vary linearly with it, as shown by Table 9 and Fig. 3, the correlation coefficient obtained by least-squares treatment of the results exceeds 0.96.

We shall note immediately that there exist apparently two $E = f(\Sigma I_r)$, straight lines, one (D_1) referring to moieties incorporating only double and triple bonds and the other (D_2) describing mixed moieties.

Table 9.

P { >C=C< $E=0$ $\Sigma I_r=1.464$; —C≡C— $E=0$ $\Sigma I_r=1.464$

(D_1) straight line	E	ΣI_r	(D_2) straight line	E	ΣI_r
(α)—C≡C—C≡C—	+ 77	2.136	(D) >C=C—C≡C—	+ 63	2.494
(β)>C=C—C=C<	+121	2.509	(E)—C≡C—C≡C—C=C<	+ 98	2.926
(γ)>C=C—C=C—C=C<	+211	3.476	(F) >C=C—C=C—C≡C—	+141	3.574
(δ)N≡C—C≡C—C≡N	+ 40	1.836	(G)—C≡C—C=O	+ 12	1.882
(ε)—C≡C—C≡N	+ 40	1.840	(H)>C=C—C≡N	+ 40	2.093
(μ)>C=C—C=O	+ 44	1.843	(J)O=C—C≡C—C=O	+ 50	2.286

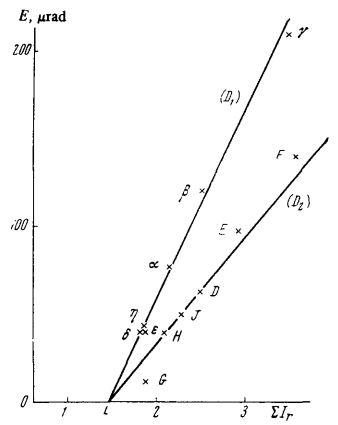


Figure 3.

This difficulty undoubtedly shows that the method of calculation employed (the Hückel approximation) does not allow a description of the second case with the same rigour as the first. In fact the calculation does not take into account a significant interaction between π-electron systems and the π-electron system of the triple bond, when it is conjugated with a double bond, which leads to low values of the bond indices and an appreciably high value of the sum of the free valence indices. Evidently, a more refined method of calculation would yield for compounds with mixed moieties a lower sum of the free valence indices compared with the values in Table 9, which would shift the points on the (D_2) straight line to the (D_1) line. Therefore, we shall subsequently place greater reliance on the coefficients corresponding to (D_1) and we will employ only these in all our discussions. Before proceeding to further exposition, we must make a small detour. The physical chemist, observing empirically a simple relation between

the measured quantity and some theoretical parameters, can adopt two attitudes: he can either take the risky course of remaining blissfully satisfied or he can attempt to show that the relation obtained is in no way due to chance. The first attitude was in fact ours until we decided to adopt the second. More precisely, we adopted this point of view when we were able to show that the magnetic rotation of buta-1,3-diene is a linear function of a sum of the type $\Sigma c_i c_j$ (c_i and c_j are the coefficients of non-adjacent atomic orbitals in molecular orbitals), a sum which represents none other than the ineffective bond indices in the molecule, i.e. the free valence indices. This is valid with sufficient rigour only for aliphatic systems, which we shall call "unsubstituted", where the atoms of the conjugated moiety are linked only to hydrogen or alkyl groups. In fact, it was established that a substituent X other than those mentioned above alters E and ΣI_r to such an extent that the (D_1) straight line cannot be used[62]. However, despite this, one may attempt, by continuing to develop our concepts, to obtain from the data for the Faraday effect extremely interesting results. For example, if we examine a family of compounds of the type R–C=C=C(X) [sic! (Editor of Translation)] (where X = H, CH_3, Cl, OR, or NH_2), it is evident that E varies appreciably as a function of X (Table 10). This is also valid for the series of α-unsaturated carbonyl compounds (Table 11).

Table 10.

Compound	E, μrad	p_{23}
R–C≡C–C(H)=O	18	0.247
R–C≡C–C(R')=O	12	0.240
R–C≡C–C(OH)=O	25	0.262
R–C≡C–C(Cl)=O	17.5	0.247
R–C≡C–C(NH_2)=O	5	0.232

Castan's classical calculation[63-66] of the π-electronic structure by Julg's method shows that the observed changes in E can be related in both cases to changes in the indices of the "single" (C_2–C_3) bond by expressions of the type

$$E_e = 940\, p_{23} - 253,$$
$$E_a = 810\, p_{23} - 183.$$

The first is valid for ethylene derivatives and the second for acetylene derivatives[67]. The relations are of definite interest from the standpoint of both the Faraday effect and quantum chemistry.

1. They throw light on the apparently random distribution of E values obtained from experimental observations and indicate the extreme sensitivity of the Faraday effect to minute changes in the electronic characteristics of conjugated molecules: thus in ethylene derivatives Δp_{23} of the order of 0.04 of an electron corresponds to a change ΔE of the order of 35 μrad.

2. They make it possible to predict the numerical value of the magnetic rotation for those compounds of the type investigated for which experimental data are not available.

3. They permit a refinement of the Couloumbic integrals and the effect of the substituent X when these are not known with adequate precision. In particular, Castan confirmed the integrals proposed by Peradjordi[68] for the amide group, whereas in the literature there exist discrepancies on this question.

4. Finally, they demonstrate the existence of a definite threshold, in terms of bond indices, beyond which conjugation effects must not be expected in the Faraday effect, namely for ethylene derivatives starting with 0.269 and for acetylene derivatives starting with 0.226.

This unusual result suggests that in an unsaturated system there may be electron delocalisation which is not reflected in the Faraday effect, i.e. the deformation of molecular orbitals under the influence of the magnetic field is too insignificant for observation. The existence of a threshold accounts for the zero exaltation of conjugation in α-diketones; although these compounds are in fact evidently conjugated, their $p_{23} = 0.152$ is significantly below the detection threshold, as shown by Castan and Labarre[69].

Table 11.

Compound	E, μrad	p_{23}
CH_2=CH–C(H)=O	45	0.296
CH_2=CH–C(CH_3)=O	19	0.288
CH_3–CH=CH–C(H)=O	43	0.315
CH_3–CH=CH–C(CH_3)=O R–CH=CH–C(CH_3)=O CH_3–CH=CH–C(R')=O	35	0.307
CH_3–CH=C(CH_3)–C(H)=O	37	0.308
(CH_3)$_2$C=CH–C(CH_3)=O	54	0.328
CH_2=C(CH_3)–C(H)=O	—	0.288

Having investigated in this way the "linear" conjugated systems, we now consider the behaviour of conjugation exaltation in cyclic systems. The idea underlying the first study in this field by Graffeuil and coworkers[70] is quite analogous to that just discussed. The study was based on a large number of hydrocarbons containing one or several benzene rings. A linear relation was observed between the conjugation exaltation E_{Ar} and ΣI_r with the same initial abscissa as for the (D_1) straight line. However, now the experimental points lie on another straight line (D_2):

$$D_1 \quad E_{Al} = 111\,(\Sigma I_r - 1.464),$$
$$D_2 \quad E_{Ar} = 200\,(\Sigma I_r - 1.464).$$

This implies that, for a conjugated system characterised by the value of ΣI_r, the exaltation E_{Ar} (for cyclic molecules) greatly exceeds E_{Al} (for alicyclic molecules).

$\Delta E = E_{Ar} - E_{Al}$ reflects to some extent the transition from conjugation in open chains to conjugation in rings or to "aromaticity". The existence of ΔE is due to the presence in the aromatic molecule of delocalised π electrons the increased mobility of which under the influence of an applied magnetic field may be observed. Thus we immediately discover that ΔE is due to the Pauling–Pople current characteristic of a cyclic molecule. This hypothesis is the starting point of an exciting study, since under these conditions the Faraday effect constitutes a cardinal method for investigating the entire problem of aromaticity. Moreover, ring currents, as an expression of the magnetic properties of the substance, are as important as the susceptibility and nuclear magnetic resonance, where, incidentally, the existence of the Pauling–Pople current was first demonstrated.

The same conjugation exaltation might also be expected for all aromatic molecules with a specified value of ΣI_r. However, if one examines for this purpose the entire multiplicity of mono- and poly-substituted benzenes, it is immediately seen that such expectation is in vain: Table 12 lists certain values of E obtained in a number of investigations [71-76] and readily shows small deviations upwards and appreciable deviations downwards from 182 μrad, which is characteristic of benzene. It is also evident that for all such molecules ΣI_r remains virtually constant, at least when the calculation is performed in the same way with respect to the benzene ring. The question arises as to the factor, electronic or geometrical, which has such a marked influence on the conjugation exaltation of the molecule and its aromaticity. An answer was obtained after the investigation of the $(\sigma + \pi)$ electronic structures of 60 substituted benzenes, which we calculated ourselves [77-80].

Table 12.

№*	E, μrad	G	№*	E, μrad	G
6	208	0.006	*23*	147	0.030
1	191	0.031	*16*	147	0.059
20	187	0.016	*24*	137	0.063
8	183	0.066	*17*	130	0.109
21	177	0.037	*19*	125	0.081
14	176	0.029	*7*	123	0.088
3	175	0.032	*2*	91	0.112
4	170	0.083	*11*	66	0.144
10	166	0.064	*5*	63	0.138
12	152	0.101	*15*	59	0.101
9	150	0.071	*13*	25	0.169
18	148	0.063	*22*	12	0.159

*The numbering corresponds to the curves in Fig. 4.

The methods of calculation employed were similar [48,77]. One may conclude that, whereas the bond indices are always close to the value (0.667) observed for benzene, the gradient of the $(\sigma + \pi)$ electronic charge localised at the six carbon atoms in the benzene ring deviates more or less appreciably from the zero value which obtains in benzene (Table 12). The charge gradient gives rise to potential barriers at the vertices of the ring, reducing the ability of delocalised π electrons to generate the ring current. It was found that, although the aromaticity of the molecule does evidently depend on the π-electron density, it is also a function of the distribution of σ-electron density. Thus we arrive at Musher's objection to the concept of the ring current, at least in its classical form. The results of our magneto-optical studies show that the molecule can have a high delocalised electron density and nevertheless have no ring current, provided that the gradient G is sufficiently large.

Fig. 4 confirms the validity of the foregoing, since it reveals a very important linear relation between E and G. [81] It should be noted that the definition of G is quite independent of the nature of the atoms in the molecule. Clearly, this quantity can be calculated with equal success for both hydrocarbons and heterocycles, for example pyridine, and for heteroatomic cyclic compounds, for example borazine. Subsequently we shall find it very important to be able to measure the relative aromaticity of the molecule under specified conditions in terms of the quantity G, i.e. to be able to use the same concept to describe both benzene homologues and heterocycles of the same symmetry; this makes it unnecessary to introduce the concept of pseudoaromaticity, so frequently encountered in the literature, when a heteroatom replaces a carbon atom in the ring.

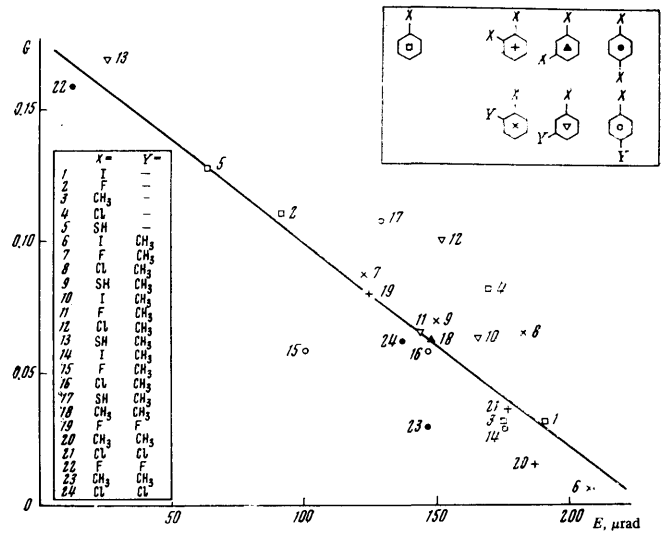


Figure 4.

The sum total of the results led us to the following definition [82]: a cyclic molecule is aromatic when the distribution of the delocalised π electrons is such that they can be put in motion under the influence of an applied magnetic field [in consequence of the absence of an appreciable gradient of the $(\sigma + \pi)$ charge localised at the vertices of the molecule]. The Pauling–Pople current then arises. This aromaticity can be either measured experimentally with the aid of the Faraday effect (the measured E) or predicted theoretically by calculating the $(\sigma + \pi)$ electronic structures (the definition of G and p_{rs}). Thus we have two equivalent means for determining to what extent the molecules belong to a particular type, provided of course that the charge distribution along the ring belongs to the same symmetry group. This conclusion follows from the following observation: when E is expressed as a function of G for compounds belonging (in the sense just described) to the D_{3h} group (borazines and boroxins) [83-85] or to the C_{2v} group (furan, thiophen, etc.) [86], we obtain in each case a linear relation—the corresponding graph is parallel to that shown in Fig. 4. However, for each group the symmetry of the distribution of the localised $(\sigma + \pi)$ charge (at the vertices of the ring), there exists a specific $E = f(G)$ straight line which cannot be made to coincide with the line in Fig. 4 whatever assumptions are made in the calculation. Thus we arrive at Musher's second objection to the ring current. It largely recapitulates the previous postulate.

1. It is impossible to compare the aromaticities of benzene and a molecule which does not belong to the D_{6h} group. Even if we are entitled to measure the aromaticities of substituted benzenes relative to that of benzene itself, this can only be done provided the Coloumbic integrals, correctly estimated from ultraviolet spectra, show

only small deviations from the value of α, as for X = P, Cl, I, and SH; on the other hand, for aminobenzenes we obtain from the ultraviolet spectra $\alpha C(NH_2) = \alpha - 0.6\beta$,[87] which corresponds to a C_{2v} symmetry of the benzene ring rather than D_{6h}.

2. It appears that certain benzene derivatives cannot be classified as aromatic compounds at all. In particular, this applies to fluorobenzene, which has an extremely low value of E_{Ar}, lower than that which benzene should have if it were "aliphatic", i.e. if the ring current were altogether absent. Clearly, we hesitated for a long time before publishing such a surprising conclusion. Our doubts continued until we recognised that fluorobenzenes are nitrated and sulphonated with difficulty‡, which may be regarded as a chemical criterion of the quasi-non-aromaticity of fluorobenzene.

We have discussed thoroughly the problem of the aromaticity of substituted benzenes. However, the rule which we have proposed is evidently general: we have used it also to solve the problem of the aromaticity of substituted borazines and boroxins of D_{3h} symmetry—the problem which has been the subject of controversy, as shown by the literature. We calculated the $(\sigma + \pi)$ electronic structure of molecules of this type, the magnetic properties of which have been investigated systematically by Laurent and coworkers[88-91] and the relative aromaticity scale, which we obtained using the calculated values of G, is very satisfactorily confirmed by experimental data[92].

The concept of aromaticity in terms of our definition was then applied[86] to pentagonal heterocycles of the C_{2v} group. The data obtained yielded the familiar result that pyrrole and furan are virtually non-aromatic, while thiophen is aromatic owing to overlapping of the 3d orbitals of sulphur, which promotes the appearance of a ring current.

We showed that the aromaticity of pyridine is 5–6 times lower than that of its N-oxide[93]. This becomes clear after examining the structure of the (N→O) donor–acceptor bond, which reduces the electron density at the nitrogen atom, while its enhanced value in pyridine is responsible for the potential barrier which prevents the occurrence of a ring current.

Finally, Bonnafous[94] investigated the aromaticity of nitrobenzenes and nitrotoluenes[94]. However, this problem, which is associated with the nature and magneto-optical properties of coordination bonds, will be set aside for discussion in the appropriate section.

Another magneto-optical criterion of aromaticity, for which we had great hopes in 1967 bearing in mind its operational simplicity, was discussed similarly. This criterion was suggested by Zimmerman and Foster's NMR experiments[95]: they showed that the signal due to benzene protons is displaced towards weaker fields on diluting benzene with a chemically inert solvent and Pople suggested that this may be due to a change in the ring current on dilution[96]. A similar experiment by Crasnier on the Faraday effect showed that the molecular magnetic rotation of benzene decreases exactly linearly on dilution by a solvent such as hexane. We believed that we had a simple means for measuring the "intensity" of the ring current in the molecule and became even more firmly convinced of this after a study[82] showing that the corresponding decrease in the above solvents is greater the greater is the initial "intensity". The first measurements for fluorobenzene, p-difluorobenzene, chlorobenzene, and bromobenzene, in n-hexane solution[82] enabled us to establish a relative aromaticity scale identical with that which is deduced from the measurements of E and calculations of G. However, this agreement gradually disappeared as the number of molecules investigated increased and soon it was necessary to conclude that the straight line obtained for a given aromatic compound (see iodobenzene[80]) varies from one solvent to another so much that we are simply unable to take into account the solute–solvent chemical interaction. Precisely because of these considerations, we undertook a new study of the criterion of aromaticity "in solution" by measuring the molecular rotation of benzene in 16 solvents; the results[97] are presented in Fig. 5 and in Table 13.

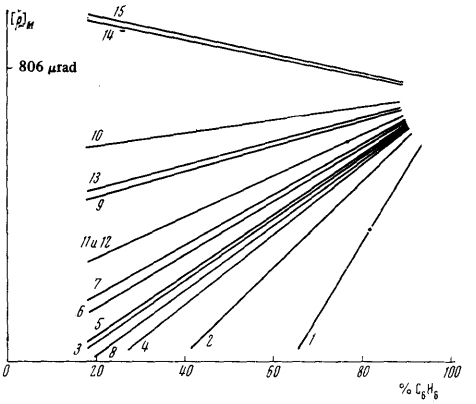


Figure 5.

Table 13.

No.	Solvent	Equation	r	n_D^{20}	P
1	Trifluoroethanol	$y=0.856\ x+730.3$	0.99	1.2910	0.182
2	Methanol	$y=0.498\ x+762.8$	0.99	1.3288	0.203
3	Ethyl ether	$y=0.346\ x+773.8$	0.99	1.3526	0.217
4	Ethanol	$y=0.399\ x+771.5$	0.99	1.3611	0.221
5	n-Hexane	$y=0.338\ x+773.0$	0.99	1.3749	0.229
6	Isopropyl alcohol	$y=0.294\ x+779.2$	0.98	1.3776	0.230
	1-Propanol	$y=0.287\ x+781.0$	0.99	1.3850	0.234
7	Iso-octane	$y=0.358\ x+773.4$	0.99	1.3915	0.238
8	Tetrahydrofuran	$y=0.140\ x+794.0$	0.96	1.4076	0.247
9	Dioxan	$y=0.072\ x+801.9$	0.95	1.4224	0.254
10	Cyclohexane	$y=0.229\ x+787.2$	0.99	1.4266	0.257
11	Dimethyl formamide	$y=0.231\ x+788.9$	0.97	1.4269	0.257
12	Chloroform	$y=0.130\ x+798.3$	0.99	1.4433	0.265
13	Carbon tetrachloride	$y=-0.103\ x+818.5$	0.97	1.4601	0.274
14	Dimethyl sulphoxide	$y=-0.111\ x+819.9$	0.99	1.4780	0.284

*The numbering corresponds to the curves in Fig. 5.

They require the following comments. (1) The variation of $(\rho)_M$ is exactly linear over a wide range of concentrations, which is confirmed by the correlation coefficients r; (2) however, the decrease observed for hexane, on which earlier we intended to base the criterion of aromaticity in solution, is by no means general—in particular, it is evident that in certain cases there is an increase and not a decrease of $(\rho)_M$; (3) as regards the order in which the solvents investigated can be arranged, it is at first sight difficult to grasp whether, for example, their macroscopic

‡ Electrophilic substitution reactions of fluorobenzene (including nitration) are well known, see, for example, Stock and Brown[186] (Editor).

polarisability is an appreciable factor or not—from this point of view it is surprising that carbon tetrachloride and dimethyl sulphoxide give similar experimental relations.

It is customary to say that the solute–solvent interaction depends directly on the polarity and the polarisability of the components of the system under consideration. Bearing this in mind, it was logical to check whether the changes in $(\rho)_M$ are a function of polarisability. For each solvent, we calculated the molecular polarisability P from the Lorentz formula

$$P = \frac{(n_D^{20})^2 - 1}{(n_D^{20})^2 + 2}$$

and showed (Fig. 6) that there is a significantly linear relation between P and the experimental data for the Faraday effect[97]. However, it is evident that the decrease of $(\rho)_M$ does not depend directly, as might have been expected, on the "intensity" of the ring current in the molecule when the substance is diluted but is more likely to be associated with solute–solvent interactions, which cause a more or less pronounced change in the internal electric field. The overall effect of the internal electric field and the external magnetic field is in fact observed. Hence one must assume that the investigation of "aromatic" molecules in solution by the magneto-optical method cannot yield a criterion of aromaticity. However, this conclusion must be extended also to the results of analogous NMR studies, as suggested simultaneously both by our group[67] and by Falk and coworkers[98].

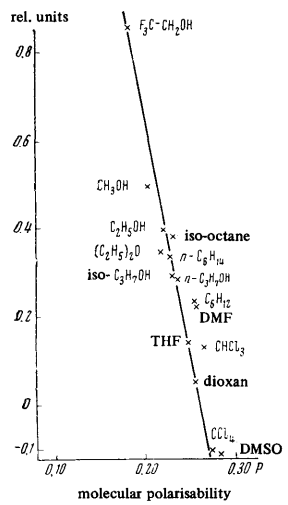


Figure 6.

Some Comments on the Term Aromaticity

We have just seen that measurements of the Faraday effect on the one hand and the knowledge of electronic structures on the other permit the determination of the relative aromaticity of the molecule by a method which is extremely similar to that employed in NMR, i.e. on the basis of the ring current concept.

However, it is quite evident that aromaticity does not always imply the presence of a ring current. Organic chemists will recall the tendency of the molecule to undergo nitration and sulphonation, while to others aromaticity implies the equality of bond lengths, high stabilisation energy, enhanced diamagnetic anisotropy, ultraviolet absorption very close to the visible region, and finally intense spin delocalisation (in ions and radicals). Nevertheless, it appears clear that the word aromaticity has lost any kind of simple significance and that we are unable to give it a true definition. An additional difficulty arises because we cannot measure the aromaticity of the molecule and even relative scales based on the measurements of various chemical and physical properties are not absolutely consistent.

From our standpoint, the time has now come to reject the use of the term aromaticity in order to eradicate from speech and print the ambiguity which consists in the postulate that "aromatic means benzene-like and conversely". In fact we have already seen that certain substituted benzenes characterised by a low value of E and a large gradient G cannot be classified as aromatic. Our suggestion that the term aromatic be rejected should also be welcomed because there exist numerous prefixes (non-, anti-, quasi-, pseudo-, homo-, ...) to this term. Clearly "the time is now right" for this. However, as mentioned by Coulson[99], the problem does not consist in finding a new word to replace the term aromaticity: it appears preferable to introduce a series of new concepts such that each should refer to one of the numerous chemical or physical properties the sum of which makes it possible to comprehend the essential features of aromaticity. On the basis of these considerations, we suggest that the concept of "potential strobilism" be adopted to describe the property measured both in connection with the Faraday effect and in NMR in studies on planar cyclic molecules with delocalised π electrons, i.e. when there is a ring current. Thus the strobilism has a potential existence in the molecule and can be discovered by the investigator by applying an external magnetic field. Since the strobilism is a potential property of the molecule in an unperturbed state, one may postulate a direct relation between it and the electronic and geometrical characteristics of the ground state: the distribution of both σ and π electrons, group symmetry, etc.

In conclusion[81] we should like everyone to be clear about the essential nature of our demarche: physicists and chemists observe different effects of "aromaticity"—a pleasant smell, capacity for nitration and sulphonation, a ring current, magneto-optical exaltation, and diamagnetic resonance energy (incidentally this is more of a mathematical term). However, no one can answer the problem whether or not these are consequences of the same property.

In the first place it is extremely desirable to define and express quantitatively the information which each particular method can yield. The various refined concepts will be combined spontaneously provided this is possible in principle.

VI. THE FARADAY EFFECT AND THREE-DIMENSIONAL CONJUGATION

We have already seen that the Faraday effect makes it possible to observe and analyse very refined phenomena of classical electronic delocalisation. However, it must

be emphasised that other methods also allow this—naturally with varying success. However, there is one field where the magnetic rotation of polarisation occupies a privileged position and we should like to devote a few lines to this. Whilst attending in 1967 a seminar in Paris held by Prof. Heilbronner, we heard for the first time of the phenomenon of "three-dimensional conjugation". The exceptionally unusual ultraviolet spectroscopic behaviour of 5,6-diphenylnaphthacene or rubrene was discussed: it exhibits an anomalously large bathochromic shift compared with naphthacene, although it is known that owing to steric hindrance the phenyl groups in the 5- and 6-positions are virtually perpendicular to the plane of the polyacene. It followed from the discussion that the magnitude of the observed effect can be accounted for only by the axial overlapping of the $2p_z$ orbitals of the benzene rings, which imparts to the molecule a three-dimensional resonant structure. We immediately wished to discover whether or not this phenomenon can be observed by means of the Faraday effect and, apart from rubrene, concentrated attention on simpler molecules where three-dimensional conjugation might be expected on general grounds—for example cyclo-octatetraene. This compound exists in the form of a "tube" with D_{2d} symmetry; the carbon–carbon bonds are alternately 1.50 and 1.35 Å long, which indicates the absence of delocalisation of the ring π electrons. Thus, using the general relations of the Faraday effect, we should obtain an experimental molecular magnetic rotation lower than or at least equal to the theoretical value (821 μrad) obtained from additivity. However, in fact the experimental rotation (1008 μrad) exceeds by 187 μrad the expected value. In the present state of our knowledge, such appreciable exaltation of the magnetic rotation compared with the value observed for benzene (182 μrad) can only be explained by three-dimensional conjugation analogous to that in the case of rubrene. Together with Chalvet[100], we succeeded in showing that this kind of exaltation of the Faraday effect corresponds to an overlap integral $S(2p_\sigma, 2p_\sigma)$ smaller approximately by a factor of 2 than for rubrene. This agrees satisfactorily with the intramolecular distances in the compounds under discussion.

Preliminary results of this kind led us to attempt the use of the Faraday effect for the solution of problems in conformational analysis. There are no literature data on the geometrical structure of cyclo-octa-1,4-diene at 20°C. This molecule can exist either in the chair or in the boat form or can oscillate rapidly between them. However, the experimental molecular magnetic rotation is exactly equal to the theoretical value and apparently suggests that cyclo-octa-1,4-diene is planar at 20°C. This is one of the most exciting fields of study for the Faraday effect. So far we have not investigated classical molecules with a geometry allowing possible three-dimensional conjugation (we may refer to Daudel[101]) in view of the lack of the necessary specimens. We hope that our readers will include chemists who will become interested in the possibility of investigating three-dimensional conjugation using the Faraday effect and will be kind enough to get in touch with us in connection with this problem.

VII. DONOR–ACCEPTOR σ-BONDS

Previously we considered in detail how electron delocalisation in diamagnetic compounds containing only normal covalent bonds influences the Faraday effect. Deviations from additivity are observed also when one is dealing with a molecular structure containing a coordinate bond and we shall now discuss the most important features of this phenomenon. As early as 1957, Laurent was the first to undertake a series of studies[102–105] on the electronic nature of the coordinate bonds in compounds of boron halides (Lewis acids) with bases. Complexes of this type should indeed be investigated first, since they provide a rare example of a coordinate bond of purely σ type. Gallais and Laurent suggested that the formation of a $(D^+ - {}^-A)$ coordinate bond (using Lowry's notation) between a base (LMND) and an acid (XYZA) be characterised in terms of the magneto-optical constant equal to the difference $\Delta\rho$ between the molecular magnetic rotation of the complex and the sum of the molecular quantities referring to the pure initial compounds:

$$\Delta\rho = (\rho)_M(\mathrm{LMND^+ - {}^-AXYZ}) - [(\rho)_M(\mathrm{LMND}) + (\rho)_M(\mathrm{AXYZ})] .$$

Table 14.

Compound	Δρ, μrad	Compound	Δρ, μrad
$F_3B \cdot NR_3$	−506	$R_3Al \cdot PR_3$	− 94
$Cl_3B \cdot NR_3$	−140	$Br_3Al \cdot PR_3$	+ 79
$F_3B \cdot PR_3$	−535	$R_3Al \cdot OR_2$	+ 17
$Cl_3B \cdot PR_3$	−164	$Br_3Al \cdot OR_2$	− 33
$F_3B \cdot OR_2$	−350	$R_3Al \cdot SR_2$	+ 49
$Cl_3B \cdot OR_2$	− 23	$Br_3Al \cdot SR_2$	+ 86
$F_3B \cdot SR_2$	−350	$R_3Ga \cdot NR_3$	−130
$Cl_3B \cdot SR_2$	− 26	$R_3Ga \cdot PR_3$	−200
$Br_3Al \cdot NR_3$	−234	$R_3Ga \cdot OR_2$	− 85
$Br_3Al \cdot NH_3$	+ 35	$R_3Ga \cdot SR_2$	− 52

The important findings arising from such a treatment are the virtually permanently negative sign of $\Delta\rho$ and its large absolute value (Table 14). The analogous studies for aluminium compounds by Gallais and de Loth[31] and for gallium compounds by Laurent et al.[106] made it possible to extend the initial conclusions. Usually the absolute values obtained for $\Delta\rho$ were lower than those measured by Laurent for complexes based on BF_3. The authors concluded that, when a covalent bond leads to a negative value of the magneto-optical constant as defined above, the most likely reason is donor–acceptor interaction. At the same time it is evident that $\Delta\rho$ reflects not only the rotation due to the donor–acceptor bond but also the magneto-optical effect associated with all the changes occurring when the donor atom is attached to the acceptor atom. We endeavoured to separate the various factors contributing to $\Delta\rho$ and attempted to specify in each case the corresponding effects in order to isolate in a pure form from $\Delta\rho$ the magnetic rotation $\rho(D^+ - {}^-A)$ due to the donor–acceptor bond[107]. This is particularly necessary, since the negative sign of $\Delta\rho$ does not correspond to the formation of diamagnetic complexes. It has been shown[108,109] that purely magnetic rotation due to the $(D^+ - {}^-A)$ σ bond should be positive. The considerable decrease of magnetic rotation is due to secondary effects in the formation of such a bond. A complete examination of the secondary factors governing the change $\Delta\rho$ leads not only to an estimation of the purely magnetic rotation due to $(D^+ - {}^-A)$ bonds but also to a fairly complex analysis of the coordination phenomenon as a whole. More precisely, the postulate that $\rho(D^+ - {}^-A) \geqslant 0$ makes it necessary to estimate in each specific case the importance of the secondary factors and poses the problem of the multiplicity of the $(D^+ - {}^-A)$ bonds.

The most permanent of the secondary factors which may be taken into account directly in the Faraday effect is the marked decrease of the magnetic polarisability when a free electron pair of the donor atom is converted into an electron pair involved directly in bond formation. This is particularly important since donor–acceptor bonds are usually characterised by considerable charge transfer [110,111]. This marked decrease of polarisability, which leads to a decrease of the magnetic rotation in certain cases, is sufficient to account for the negative sign of $\Delta\rho$. As an example, we shall consider the compounds $R_3Al.PR_3$ ($\Delta\rho = -94$ μrad). We know the contribution $\rho(d\mathrm{P})$ by the free electron pair of the donor atom (+255 μrad) assuming sp^3 hybridisation of the phosphorus atom [39]. Assuming that at the instant of formation of the complex, the free electron pair is replaced by the paired bonding electrons, we find that the rotation due to the ($P^+-{}^-Al$) bond is

$$\Delta\rho = 255 + \rho(P^+-{}^-Al) = -94 \ \mu\text{rad},$$
$$\rho(P^+-{}^-Al) = -94 + 255 = +161 \ \mu\text{rad},$$

i.e. is positive.

Table 15.

Compound	$-\rho(d_P)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$R_3Ga\cdot OR_2$	0	−85	0	0	− 85
$R_3Ga\cdot NR_3$	− 86	−85	0	+ 41	−130
$R_3Ga\cdot PR_3$	−255	−85	0	+140	−200
$Cl_3B\cdot OP_2$	0	−23	0	0	23
$Cl_3B\cdot SR_2$	− 52	−23	0	+ 49	− 26
$Cl_3B\cdot PR_3$	−255	−23	0	+114	−164

However, the above considerations are not sufficiently general, because many factors which frequently play a major role have not been taken into account. For the case of a purely σ donor–acceptor bond, we shall recall the most important of these: (a) the formation of the complex is frequently accompanied by a change in hybridisation and in the partial ionic character; we shall denote this by δG in order to recall the change in the symmetry group; this applies equally to a Lewis base and acid; (b) the multiplicity of the normal covalent bond (π_{AXYZ} and π_{DLMN}) in isolated donor and acceptor molecules is also altered at the instant of the formation of the complex§. Table 15 shows how important are these two factors. We shall consider initially the compound R_3GaOR_2 for which $\Delta\rho = -85$ μrad. Then, as incidentally for all complexes containing an ($O^+-{}^-A$) bond, one may postulate that the electron pair of the oxygen atom is involved in the formation of this bond and hardly plays any [other] part; earlier we concluded that even the magnetic rotation due to the lone electron pair of the oxygen atom is close to zero [39]. In this situation [all the (GaR) bonds are undoubtedly single] one must postulate that the decrease of the magnetic rotation in the Faraday effect expressed by $\Delta\rho$ can only be due to factor a [when $\rho(O^+-{}^-Ga) \geqslant 0$ is postulated]. Essentially the sp^2 hybridisation of the gallium atom in GaR_3 monomer becomes close to the sp^3 hybridisation in the complex. This change is accompanied by a decrease in the polarisability of the (Ga–C) σ bonds, which, as we have shown earlier, always reduces the magnetic rotation. Expressing this by

$$(|\delta G|^{C_{3v}}_{D_{3v}}),$$

we find that in this case $\delta G = -85$ μrad.

If we consider further other gallium compounds ($R_3Ga.PR_3$, $R_3Ga.NR_3$), the use of the value of δG obtained for the second factor and the magnetic rotations due to the lone electron pairs of the phosphorus (about 255 μrad) and nitrogen (about 86 μrad) atoms yields positive values for the true rotation due to the ($P^+-{}^-Ga$) and ($N^+-{}^-Ga$) bonds¶. Similar considerations apply also to the compound $Cl_3B.OR_2$, for which $(\delta G|^{C_{3v}}_{D_{3h}}) = 2-23$ μrad†. In general this result is consistent with the higher magnetic polarisability of the (Ga–X) bond compared with (B–X). If we now substitute the value −23 μrad in the expression for $\Delta\rho$ for the compounds $Cl_3B.SR_2$ and $Cl_3B.PR_3$, we obtain for the true magnetic rotation due to the ($S^+-{}^-B$) and ($P^+-{}^-B$) bonds positive values of ρ (+49 and +114 μrad), which are lower than the corresponding contribution $\rho(d\mathrm{S})$ and $\rho(d\mathrm{P})$ due to the lone pairs.

The effect of the factor b (the multiplicity of the bonds in isolated molecules of the donor or acceptor) is clearly shown in complexes based on BF_3. It has long been known that $\Delta\rho$ for such complexes is much higher than for the analogous complexes with BCl_3. [102]

Table 16.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$F_3B\cdot OR_2$	0	−23	−327	0	−350
$F_3B\cdot SR_2$	− 52	−23	−327	+32	−370
$F_3B\cdot PR_2$	−255	−23	−327	+70	−535

Table 16 shows how $\Delta\rho$ may be used to obtain the constants for the ($D^+-{}^-A$) bonds for certain BF_3 complexes. Assuming that to a first approximation the factor

$$|\delta G|^{C_{3v}}_{D_{3h}},$$

is constant for both BF_3 and BCl_3, the formation of $F_3B.OR_2$ will differ from that of $Cl_3B.OR_2$ only due to the disappearance of the double bond character of the (F–B) bonds on transition from the isolated BF_3 molecule to the complex‡. This process leads to a decrease of the magnetic rotation by 327 μrad, which agrees only in order of magnitude with the real rotation (416 μrad) observed, for

§ The bases NR_3, PR_3, OR_2, and SR_2 have been investigated; evidently π_{DLMN} is zero in all cases. We also suggest that δG is negligibly small for these bases, because there is virtually no change in hybridisation.

¶ For example $\rho(N^+-{}^-Ga) = \Delta\rho + \rho(d_N) - \delta G = -130 + 86 + 85 = +41$ μrad.

† When the multiplicity of the (B–Cl) bond in an isolated BCl_3 molecule is neglected.

‡ The considerable double bond character of the B–X bond has been confirmed by the large changes in the asymmetry parameter ($\eta = 45\%$ for B–Br and $\eta = 45\%$ for B–I in BX_3 with respect to X, which corresponds to amounts of double bond character of 13.3 and 15.6%) [127,188] (Editor).

example, for $R_nBF_{3-n}.NR'_3$.[112] Thus we have to recognise the existence in this case, as incidentally also in certain others discussed below, of a third factor responsible for the high negative value of the observed $\Delta\rho$. We now substitute $\pi_{BF_3} = -327$ μrad in the expression for $\Delta\rho$ for the compounds $F_3B.SR_2$ and $F_3B.PR_3$; this leads to positive values of $\rho(S^+-{}^-B)$ and $\rho(P^+-{}^-B)$ lower than the corresponding $\rho(d_S)$ and $\rho(dp)$. It is interesting to note that the results for the $(P^+-{}^-B)$ bond were obtained[113] from a study of the magneto-optical properties of the compounds $H_3B.PR_3$ by means of an analysis which differs significantly from that described above. In the compounds investigated $\Delta\rho \simeq -480$ μrad and the relative contributions by factors which must be taken into account are $-\rho(d_P) = -255$ μrad, $(\pi_{AXYZ}) = 0$, and $-\delta G = -300$ μrad. The resulting value of the modulus $\rho(P^+-{}^-B)$ is positive (+85 μrad) and is the same as that found from a series of $F_3B.PR_3$ compounds. Nevertheless there is a significant difference between the contributions of the factors constituting $\Delta\rho$ on passing from $F_3B.PR_3$ or $Cl_3B.PR_3$ to $H_3B.PR_3$: in the latter case the δG term is very large, so that the homopolarity of the (B–H) bond entails a high value of the b_{BH} coefficient[50] and a large change in it on passing from the hypothetical BH_3 molecule to the BH_3 group in the real complex. In conclusion of the first part of the discussion, we may note that we appear to be in a position to explain in specific cases the order of magnitude of the factors contributing to $\Delta\rho$ assuming that the contribution by the donor–acceptor bond in the compounds investigated is positive. The problem of the multiplicity of this bond has clearly remained outside the discussion. The observed large negative values of $\Delta\rho$ can be reasonably accounted for by factors characterised by the negative quantities $-\rho(d_D)$, $-\pi_{AXYZ}$, and $-\delta G$, the last sometimes predominating.

Table 17.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)+\pi$	$\xi(D\cdot A)\ \Delta\rho$
$R_3Al\cdot OR_2$	0	−50	0	+ 67	+17
$R_3Al\cdot SR_2$	−52	−50	0	+151	+49
$R_3Ga\cdot SR_2$	−52	−85	0	+ 85	−52

The general analysis would have to be continued further if there existed a theoretical possibility of a multiple donor–acceptor bond. In the series of compounds in which we are interested such a possibility would exist theoretically if the d orbitals of the acceptor atom could effectively overlap the sp^3 hybridised orbitals of the donor atom. For boron–oxygen and gallium–oxygen bonds, this is excluded on energetic grounds, but is possible for aluminium–oxygen, aluminium–sulphur, and gallium–sulphur bonds. We shall consider from this standpoint the $(O^+-{}^-Al)$ bond in $R_3Al.OR_2$ (Table 17). One lone electron pair on the oxygen atom is involved in the formation of the donor–acceptor bond and the other occupies the $(2s, 2p)$ hybrid orbital, which cannot overlap the $3d$ orbitals of the aluminium atom on symmetry grounds. However, the overlap integral $S(2p, 3d)$, although small (of the order of 0.5 eV) is not zero. Bearing in mind the previous postulates $[\rho(d_0) = 0]$, it follows that $[\rho(O^+-{}^-Al) = 0]$, and, assuming that $\delta G\left|{}^{C_{3V}}_{D_{3h}}\right.$ should be about −50 μrad, we find from the interpolation of the values obtained for boron (−23 μrad) and gallium (−85 μrad) compounds that we can write $\Delta\rho = +17 = \delta G + \pi(OAl)$, whence $\pi(OAl) \simeq 67$ μrad. This value of $\pi(OAl)$ appears to be sufficiently high to reflect some multiplicity of the O–Al bond. In any case, if the $(O^+-{}^-Al)$ bond has some multiplicity, this is even more true of the $(S^+-{}^-Al)$ bond, where the overlap integral $S(3p, 3d)$ is numerically much larger than $S(2p, 3d)$. Indeed, for $R_3Al.SR_2$,

$$\rho(S^+-{}^-Al)+\pi(SAl)=151 \quad \mu\text{rad},$$

and, assuming that the rotation due purely to $(S^+-{}^-Al)$ must be less than or at least equal to $\rho(d_S) = +52$ μrad, we arrive at $\pi(SAl)$ of the order of 100 μrad. This may be interpreted as an increase of the multiplicity of the coordinate bond in sulphur compounds which are isologous with oxygen compounds. Among gallium compounds there also exist examples where the $(D^+-{}^-Ga)$ bonds have a definite π character; this is possible for $R_3Ga.SR_2$ [from the standpoint of the overlap integral $S(3p, 4d)$]. According to Table 17, $\rho(S^+-{}^-Ga) + \pi(SGa) = +85$ μrad; assuming that $\rho(d_S) = +52$ μrad, one must postulate that $\pi(SGa)$ is at least 33 μrad.

Table 18.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\pi(D^+-{}^-A)$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$Cl_3B\cdot NR_3$	−86	−23	0	0	−31	−140
$F_3B\cdot NR_3$	−86	−23	−327	0	−70	−506

We have considered how it is possible to obtain the approximate magnitude of various factors contributing to the overall value of $\Delta\rho$, using a detailed analysis of the mechanism of the formation of the complexes. We emphasise yet again that a significant feature is the hypothesis that the actual magnetic rotation due to the δ or $(\delta+\pi)$ donor–acceptor bond must never be negative. There are, however, several examples for which analysis of $\Delta\rho$ within the framework of the assumptions made here precludes the assignment of a positive magnetic rotation to the donor–acceptor bond. Thus Table 18 shows that the data for the $Cl_3B.NR_3$ and $F_3B.NR_3$ molecules can yield negative $\rho(N^+-{}^-B)$ (−31 and −70 μrad). Possibly the calculation of $\rho(N^+-{}^-B)$ for these compounds is not sufficiently accurate because the rotation due to the (N–C) bonds in the complex differs appreciably from the corresponding value for the isolated NR_3 molecule. In reality, from the standpoint of the Faraday effect, the (N–C) bond is very sensitive even to the replacement of one R by hydrogen. For example, on going from tertiary to secondary and primary amines, there is an appreciable change in rotation[114]. Possibly the presence of the $(N^+-{}^-B)$ bond also affects $\rho(N^+-{}^-B)$, but at the present time we are not in a position to take this into account[115].

VIII. DONOR–ACCEPTOR ($\sigma + \pi$) BONDS

It is clear from the foregoing that the Faraday effect constitutes a physicochemical method which is especially sensitive in the study of donor–acceptor σ bonds on the

one hand and in the detection of π electrons (both localised and delocalised) on the other. Therefore the idea of applying this technique in the investigation of dative bonds, where there is a superposition of a donor–acceptor σ bond and one or several coordinate π bonds, in order to obtain evidence for the multiplicity of dative bonds is extremely attractive. When such a study was planned at the beginning of 1960, the literature of the period contained a relatively large number of papers where it was postulated that certain bonds are of the donor–acceptor ($\sigma + \pi$) type. We undertook an investigation with the aid of the Faraday effect in order to contribute to the solution of the problem.

A. THE (PO) BOND IN COMPOUNDS OP(XYZ)

The nature of the PO bond like that of oxygen–non-metal bonds, has been the subject of discussion in the literature from the standpoint of the currently most popular hypotheses and its treatment reflects the general ideas which are dominant at the given time. Initially this bond was thought to be double[116] but later it became described as of the donor–acceptor type when the octet concept prevailed[117]. With progress in the study of geometrical structures, it was, however, found that the (PO) bond is too short to be regarded as single and it became represented as having a definite multiple character[118], which led many investigators to the conclusion that it has double bond character. However, numerous observations are in poor agreement with this somewhat schematic concept. In particular the fact that molecular magnetic rotations of $OP(OH)_3$ and $OPCl_3$ are lower than the corresponding values for $P(OH)_3$ and PCl_3 was observed long ago by Voigt[119]. However, all our knowledge about π bonds shows that π electrons exhibit very high magneto-optical activity and therefore it is quite incomprehensible why $OP(OH)_3$ should have a smaller rotation than $P(OH)_3$ if its structure were indeed represented by the formula $O = P(OH)_3$. The same remark is valid also for any comparisons between OP(XYZ) and P(XYZ).[120] This conclusion inevitably leads to the structure O←P(XYZ) on the basis of numerous examples of complexes in which the formation of a donor–acceptor σ bond leads to an appreciable decrease of the magnetic rotation (cf. the previous section). We can now understand the causes underlying the problem formulated in this way, which we thought interesting to solve with the aid of the Faraday effect. Starting in 1961, Labarre and Voigt undertook the synthesis and magneto-optical study of a large number of compounds of the type P(XYZ) and OP(XYZ).[121–123] Initially the results were interpreted on the basis of additivity, which should obtain in tervalent phosphorus compounds (molecules with covalent diamagnetic σ bonds)[36,37]. Indeed they discovered the relation $\rho = a + bI$, which was already discussed in Section III.[51] They succeeded, together with Gallais, in employing the method involving the resolution of the magnetic rotation of the compound OP(XYZ) into bond constants in order to determine the true magnetic rotation due to the (PO) bond[36,37]. It should be noted that all the geometrical and electronic factors which must be invoked to describe the addition of the oxygen atom to the P(XYZ) molecule were rigorously defined and numerically calculated with a high degree of accuracy[124,125].

Table 19 lists the values of ρ(PO) obtained and it is immediately seen that this quantity depends markedly on the nature of the atoms or groups of atoms attached to phosphorus. It was logical to relate certain changes to the parameters which describe the real electronic structure of the ($\sigma + \pi$) bond using the classical procedure in quantum chemistry or more precisely to the multiplicity of this bond in our case. Initially we employed the results of Wagner's calculation[126], since the formal mathematical treatment was based on a model of the (PO) bond in which the σ and π bonds were treated as of the donor–acceptor type. Wagner calculated the relevant indices of the (PO) bonds, which ranged from zero for (OPR_3) to two for (OPF_3) (see Table 19).

Table 19.

Compound	p_π (Wagner's data)	p_π (authors' data)	ρ(PO), μrad
OPF_3	1.983	1.911	91
$OP(OR)F_2$	1.682	1.661	88
$OP(OR)_2F$	1.381	1.414	86
$OP(PR)_3$	1.079	1.165	82
$OP(OR)_2Cl$	1.115	0.983	77
$OP(OR)_2R$	0.720	0.778	66
$OP(OR)Cl_2$	1.151	0.621	55
$OPR_2(OR)$	0.360	0.391	40
$ORCl_3$	1.188	0.349	39
OPR_3	0	0.003	0
$OP(SR)_3$	—	0.004	0

In 1967 the existence of a simple and unambiguous relation between the true magnetic rotation ρ(PO) and Wagner's π-bond indices was demonstrated for the entire set of molecules investigated[36,37]. Although the corresponding curve had a maximum, M. C. Labarre, Voigt, and Gallais expressed doubts concerning certain experimental points.

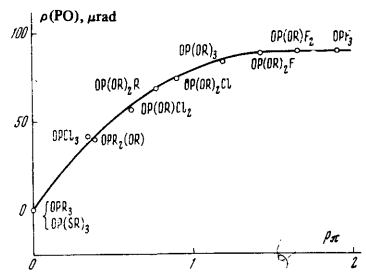


Figure 7.

Therefore Castan and Dagnac-Amans investigated in 1969[124] the electronic structure of OP(XYZ) using a formal treatment very close to Wagner's[126], but, in order to avoid a number of approximations and inaccuracies, they improved significantly the method of calculation. As in the method of Gallais and coworkers[48], the charge transferred via σ bonds was calculated using modified Pauling exponential functions[127]. The new values of the π indices are listed in Table 19 and Fig. 7 shows that the maximum about the existence of which doubts had been expressed has indeed disappeared. It is clear from the foregoing that the monotonic relation between ρ(PO) and p_π in Fig. 7 indicates that the (PO) bond is of the donor–acceptor ($\sigma + \pi$) type.

B. THE (PS) BOND IN COMPOUNDS SP(XYZ)

The hopeful result from the study of the nature of the PO bond led us to further investigation of other bonds of the $(\sigma + \pi)$ type. For example, M. C. Labarre and Voigt[128,129] made an attempt to determine the nature of the (PS) bond in the compounds SP(XYZ). The data on molecular magnetic rotation made it possible to determine the true rotation due to the (PS) bond in each case and to demonstrate a considerable variation of ρ(PS) as a function of the substituents X, Y, and Z.[36,37] Measurements of the susceptibility[130], refraction[131], and dipole moments[132] confirmed the amplitude and direction of the deviations observed in the Faraday effect but the possible relation $\rho(PS) = f(p_\pi)$, analogous to that found above for ρ(PO) still cannot be obtained in an explicit form because the method of calculation of Castan and Dagnac-Amans is unsuitable for sulphur derivatives [difficulties associated with the calculations of the overlap integrals $S(3p_S, 3dP)$]. On the other hand the multiplicity of the (SO) bond in the compounds OS(XY) and $O_2S(XY)$ can be calculated by the method of Castan and Dagnac-Amans[20,133]. The variation of the calculated bond indices is in this case quite parallel to the variation of the true magnetic rotation due to the (SO) bond, as can be seen from Table 20 and Fig. 8. It should be noted that the method of calculation itself may be better than that proposed by Moffitt in 1950.[134] The calculations showed that there is no abrupt change in the electronic nature of the (SO) bond in the compounds OS(XY) and the same bond in the $O_2S(XY)$ molecule. From the common sense point of view, one may predict that for one sulphur–oxygen bond the variation of multiplicity is a monotonic function of X and Y.[115]

Table 20.

Compound	p_π	p(SO), μrad
OSF_2	1.602	109
SO_3	0.939	134
O_2SF_2	0.908	117
SO_2	0.871	161
$OS(OR)_2$	0.667	102
$O_2S(OH)E$	0.573	99
OSCl(OR)	0.338	73
$O_2S(OR)_2$	0.268	76
$O_2S(OH)_2$	0.237	82
$O_2S(OH)Cl$	0.119	35
$OSCl_2$	0.010	39
O_2SCl_2	0.001	0

Physical chemists and especially infrared spectroscopists have for many years given most contradictory interpretations for one of the donor–acceptor $(\sigma + \pi)$ bonds, namely the (NiP) bond in the tetrahedral complexes $Ni[P(XYZ)]_4$.[135] Even if it were possible to show by various methods that the characteristics of this bond vary appreciably as a function of P(XYZ), it would still be doubtful if such changes are determined by the variation of the contribution by π electrons while, that by σ electrons remains constant, or vice-versa, or finally whether the observed effect is an overall one. In a magneto-optical study of a large number of $Ni[P(XYZ)]_4$ complexes carried out in 1967 by Cassoux and coworkers, it was assumed *a priori* that the investigation may be performed by a method analogous to that employed for the analysis of the (PO) and (SO) bonds using the results of most thoroughly tested quantum-chemical procedures. However, even Ballhausen and Gray, the most outstanding specialists in this problem[136], were unable, as far as we are aware, to obtain a result which satisfied them. Cassoux and coworkers synthesised a large number of nickel complexes and measured the Faraday effect for them[137–140], and, using the principles of additivity and numerical analysis of various geometrical and electronic factors associated with the coordination of four P(XYZ) molecules to the nickel atom, found the true rotation due to the (NiP) bond in each complex. Depending on the nature of the atoms or groups of atoms X, Y, and Z, ρ(NiP) varies. However, it was found that there are in addition deviations of the dispersion of the magnetic rotation from the normal value (the definition was given at the beginning of the review), although the first absorption band in the ultraviolet spectrum is sufficiently distant from the wavelengths observed in the Faraday effect for the complexes to be regarded as necessarily having the normal dispersion (Table 21). This anomaly is well known to specialists in the Faraday effect in the *absorption* region and is characteristic of complexes of transition elements with a high symmetry (T_d and O_h).

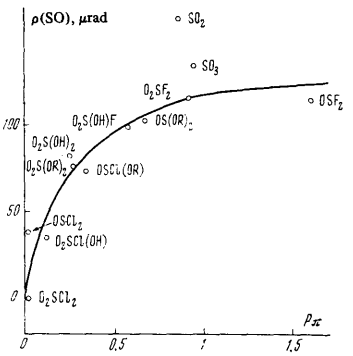


Figure 8.

Table 21.

Compound	ρ (Ni·P)	$\frac{\rho_{545}}{\rho_{578}}$	λ_{max}
$Ni(PCl_3)_4$	1266	1.20	315
$Ni[P(OR)Cl_2]_4$	1157	1.17	284
$Ni[P(OR)_2Cl]_4$	1019	1.16	265
$Ni[P(OR)_3]_4$	871	1.15	237
$Ni[P(OR)_2F]_4$	734	1.15	225
$Ni[P(OR)F_2]_4$	647	1.15	225
$Ni(PF_3)_4$	529	1.15	224

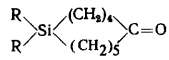
In this case the analysis must be performed not only in terms of the law of additivity but also in terms of the dispersion of the magnetic rotation.[16] Cassoux and coworkers in fact solved the problem in this way. Using Serber's formal treatment[141], they determined the dispersion curve in the region of transparency for A and B (both positive), characteristic of each of the complexes investigated. Then, using the values of A and B, they found the contributions to the magnetic rotation by the σ and π components of the

(NiP) bond[142-144]. It is significant that both contributions vary simultaneously and the multiplicity of the (NiP) bond is in all cases low and variable. These conclusions agree essentially with the results obtained by Bigorgne from infrared spectra[135].

There is yet another special case of a donor–acceptor bond to which a few lines should be devoted, namely the (NO) bond. The electronic structure of the NO_2 group was based for a long time on hypotheses involving mesomerism, i.e. the (NO) bond was regarded as simultaneously a donor–acceptor and a multiple linkage. In fact calculation in terms of such a model does not yield satisfactory results. Its authors asserted, on the basis of certain erroneous assumptions, that with its aid it is possible to obtain the correct dipole moments of such molecules as nitromethane. The reason for this was fortuitous agreement between calculation and experiment without taking into account the contribution by the lone electron pairs of the oxygen atom, which Coulson estimated to be 2D.[145] Therefore in 1967 Bonnafous continued the investigation of the electronic structure of the NO_2 group using this time not mesomeric hypotheses but the more logical Julg model[146]: the group is described in terms of a superposition of two normal (N–O) covalent bonds and a delocalised π system with four electrons: two from the sp^2-hybridised nitrogen atom and one $2p_z$ electron from each sp^2-hybridised oxygen atom. Under these conditions, LCAO calculation of the electronic structure using a calibration based on the ultraviolet spectrum[77] and an iterative procedure[48] yielded a new value of the dipole moment of the NO_2 group, in good agreement with the experimental moment, and also the corresponding absorption bands associated with the $\pi-\pi^*$ transition in the ultraviolet spectrum[147]. It follows from the results of the calculation that the (NO) bond between two atoms with markedly different charges is indeed multiple but the degree of charge transfer in the (NO) bond is 0.25 instead of 0.5 corresponding to the mesomeric concept. The Julg–Bonnafous model agrees most closely with data derived by physicochemical methods (dipole moments, ultraviolet spectroscopy, aromaticity, reactivity) for a large number of compounds, among which we may note nitroethylene[148], nitrobenzene and nitrotoluenes[94], nitropyridines[149], and others.

IX. THE FARADAY EFFECT AND CONFORMATIONAL ANALYSIS

There are certain exceptions from the law of additivity which now give rise to the possibility of investigating conformations with the aid of the Faraday effect. In this field the following important observations have been made: experimental magnetic rotation of cyclopentane, cyclooctane, cyclohexane, and their homologues (Table 22), showing deviations from additivity. In one case this maybe due to steric causes and in another to deviations from a planar structure, which are characteristic of cyclohexane derivatives with fixed carbon atoms in the ring (boat or chair). On general grounds, the decrease of magnetic polarisability in the Faraday effect must be attributed to the characteristics of the configuration, an increase in the barrier to rotation, etc. The law of systematic additivity is known to be fully valid in the absence of steric hindrance for cyclic germanium and silicon compounds with a confused conformation ("pelote).[150] In other cases the strain in the system inevitably leads to experimental magnetic rotations much lower than the theoretical values based on additivity. For example, for the compound



the interaction between the π-electron system of the (C=O) bond and the vacant 3*d* orbitals of the silicon atoms causes a 70% deviation from the theoretical additive value[150]. It is interesting to note that no deviations are observed when the silicon atom is replaced by germanium (this is consistent with self-evident considerations) or by carbon, which indicates that the intensity of the (2*p*, 4*d*) interactions is low. This result agrees fully with the literature: indeed, if the energy levels of the atomic 2*p* orbitals of the carbon atom are much lower than the corresponding levels of the 4*d* orbitals of the silicon atom, the required overlap integral is negligibly small [in particular, the interatomic distances are also large in this case; calculation shows that $S(2p_C, 4d_{Ge}) \simeq 0$]. The foregoing is fully consistent with the semiconductor properties of macromolecules of the type[151]§.

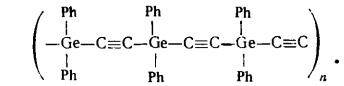


Table 22.

Compound	$[\rho]_M^{exp}$, μrad	$[\rho]_M^{theor}$, μrad	Compound	$[\rho]_M^{exp}$, μrad	$[\rho]_M^{theor}$, μrad
Cyclopentane	349	365		296	303
Cyclopentene	406	427		361	376
Cyclohexane	405	428		421	449
Cyclohexene	451	490		498	522
Cyclo-octane	570	584			
Cyclo-octene	632	646			

One can also postulate that the Faraday effect permits a clear distinction between, for example, the axial and equatorial positions of substituents in cyclohexane, as follows from the depolarisation of diffuse Rayleigh scattering. M. C. Labarre showed that the magnetic rotation of the $C_6H_{11}X$ molecule is a maximum for the equatorial configuration. For the simplest derivatives of cyclohexane, the size of the change in magnetic rotation can reach 15% (X = CH_3, Cl, OH, or NH_2). One can show that the substitution of X = PCl_2 or $P(OR)_2$ takes place preferentially in the axial position in view of the appreciable interaction of the ($P^+-{}^-Cl$) pair with the axial ($C^+-{}^-H$) pair (carbon in the 3-position)[152]. This was quite recently confirmed by electron diffraction for the compound $C_6H_{11}PCl_2$.

§ It is noteworthy that analogous compounds with silicon atoms in the chain also exhibit semiconductor properties. However, the activation energy for conduction in germanium polymers is smaller by a factor of 2 (0.6 and 1.2 eV). The conduction mechanism has still not been explained satisfactorily[189] (Editor).

At the end of the section we must emphasise that there exist two problems in conformational analysis where the Faraday effect can apparently not assist in any way: the classical *cis–trans* isomerism and hydrogen bonding. As regards the first problem, quite hopeful results were obtained by Foehr and Fenske (1949), who made measurements for 2-*cis*- and 2-*trans*-isomers of butadiene (the difference between the magnetic rotations is 7%, [153] which, according to Mulliken's treatment [154], must be attributed to the presence of *cis*- and *trans*-isomers). However, the studies by Castan [155] on a number of acids and esters of α-unsaturated acids showed that the difference between the magnetic rotations of the *cis*- and *trans*-isomers does not exceed 2%, which is quite insufficient to obtain definite results. The same may be said about the studies of hydrogen bonding by the Faraday effect method from the results of the measurements by Gallais and Wolf [156,157] on solutions of various peroxides in chloroform. They observed that the molecular magnetic rotation is insensitive to the presence of the (O...H) hydrogen bond in the series of compounds investigation. On the other hand, analysis of the aromaticity of various phenols and their ethers with the aid of the Faraday effect demonstrated its insensitivity to intramolecular hydrogen bonding.

X. THE FARADAY EFFECT AND THE STUDY OF NON-ISOLATED COMPLEXES IN SOLUTIONS

Earlier we showed that, with certain exceptions, the magnetic rotation in the Faraday effect corresponds exactly to additivity. However, this applies equally to mixtures of substances, at least when there are no solute–solvent interactions. Then, according to the Verdet law,

$$\rho = \sum_0^k \rho_k v_k \left(c \sum_0^k v_k = 1 \text{ ml} \right),$$

where ρ is the Verdet constant for the mixture of substances and ρ_k is the constant for each component. The above relation has been the subject of numerous refinements and tests; we may quote as historical references the work of Schonrock [158], de Mallemann and coworkers [159,160], Hori and Okazaki [161], and Andersen and Asmussen [162]. We may suppose that, when deviations from additivity are observed, we are dealing with chemical interactions between the various substances in the mixture. Numerous deviations from additivity observed in the work of Gallais and coworkers between 1936 and 1952 make it possible to identify and detect non-isolatable complexes, which is sometimes impossible by other methods, particularly polarography. We may point to tetraiodomercurates [163], iodobismuthates [164], thiocyanatomercurates [165–167], bismuth thiosulphates [168], bismuth(III) thiocyanates [169], etc. as examples. In this case the Faraday effect permits a reliable detection of the complex in the mixture [170,171]. The method can be also successfully employed to refine the mechanisms of the neutralisation of acids by bases [172]. Recently R_nGaCl_{3-n} complexes with aliphatic amines were successfully investigated [173].

XI. THE FARADAY EFFECT AND VAN VLECK FERROMAGNETISM

Finally we shall consider a completely specific case of deviations from additivity. It has now been known for 100 years that, despite its diamagnetism, the covalent compound $TiCl_4$ exhibits a negative Faraday effect both in the liquid [174–176] and in the vapour [177]. This is also true of $TiBr_4$. [178] However, as far as we are aware, up to 1968 no other example of molecules with an electron deficit showing an analogous behaviour in its magnetic rotation has been discovered, except for the permanganate ion [179], for which, according to the Faraday effect, a temperature independent van Fleck paramagnetism could be postulated [180]. Stone [181] showed that the positions of the ground and excited electronic energy levels explain the negative paramagnetic contribution to the magnetic rotation. For $TiCl_4$, this paramagnetic contribution may be dominant when certain postulates are made. The studies by Gervais et al. [108] on a series of covalent titanium(IV) compounds led to the conclusion that the (TiO) bond is also characterised by a negative constant for magnetic rotation and resembles in this sense the (TiCl) and (TiBr) bonds. In a study on the magneto-optical and magnetic properties of $TiCl_3OR$, Choukroun and Gervais [182] found that the $OTiCl_3$ group is responsible for paramagnetism of the van Vleck type due to the (TiCl) and (TiO) bonds. Gervais interpreted [183] additional studies on the Faraday effect in the visible region for the compounds $Ti(OR)_4$ from the standpoint of the dispersion associated with the TiO_4 group,

$$\frac{v^2}{(v^2 - v_0^2)^2}$$

in accordance with the term V_A in Serber's formula [141].

In the latest studies by Gervais and coworkers, the complexes of $TiCl_4$ [109] and $ROTiCl_3$ [184] with various alkyl orthotitanates were investigated. The study of the magneto-optical properties in the transparency range of complexes of transition elements with a high degree of symmetry must be accompanied by measurements in the absorption range. A monograph by Schatz and MacCaffery [16] deals with the Faraday effect in the absorption region.

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Thus the Faraday effect in the transparent region constitutes a characteristic physicochemical method capable of solving important problems in structural chemistry. The overall molecular magnetic rotation may be resolved on the basis of the additivity of the properties of matter into a series of components—naturally within the framework of certain postulates. An analogous assignment of various characteristic constants to definite chemical bonds is used also in other spectroscopic methods. On the other hand, all experimental deviations from additivity provide an effective means for investigating a wide variety of problems such as the delocalisation of π electrons in conjugation, the structure of donor–acceptor (σ) and ($\sigma + \pi$) bonds, molecular conformation, and finally temperature-independent paramagnetism when a transition element is involved in certain bonds.

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† Additional references supplied by the Editor.