OPTICAL ROTATORY DISPERSION

OF SOME ORGANIC MOLECULES

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Altona

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CHAPTER I

INTRODUCTION.

Natural rotatory power is since many years an invaluable aid in the study of chemical structure. Usually measurements were confined to one or two wavelengths. Although Kuhn [1] in 1929 showed the important possibilities hidden in the study of rotatory dispersion it was not until recently that a systematic exploration of these possibilities was undertaken [2] [3].

Determination of rotatory dispersion curves and of the closely related circular dichroism has already frequently rendered valuable assistance in the conformational analysis of steroids e.g. It may also supply new information about the interaction between light and molecules, from which details of electronic structure may be derived. The present thesis is meant as a contribution to this type of application.

The angle of rotation of the plane of polarization of a beam of linearly polarized light is directly proportional to the difference in refractive index of lefthanded and righthanded circularly polarized light:

$$\phi = \frac{\pi\nu}{c} (n_l - n_d) \qquad (1)$$

ϕ = angle of rotation by one cm light path in radians/cm.

ν = frequency of the light.

c = velocity of light.

n_l, n_d = refractive index of lefthanded or righthanded circularly polarized light.

A difference in absorption coefficient of lefthanded and righthanded polarized light will give rise to circular dichroism. If the difference is small, the resulting ellipticity from incident linearly polarized light is:

$$\theta = \frac{1}{4}\,(k_l - k_d) \qquad (2)$$

θ = circular dichroism (ellipticity) by one cm light path in radians/cm.

k_l, k_d = absorption coefficients by one cm light path of lefthanded and righthanded circularly polarized light.

At frequencies far enough from regions of absorption a refractive index depends on frequency according to the well known dispersion formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{Ne^2}{3\pi m} \sum_k \frac{f_{ok}}{\nu_{ko}^2 - \nu^2} \qquad (3)$$

N = Avogadro's number.
e = charge on electron.
m = mass of electron.

The summation is over the transitions of the molecule from its ground state (o) to all possible excited states (k). The oscillator strength f_{ok} is a measure of the absorption intensity at a particular resonance frequency ν_{ok}. It depends on molecular quantities according to:

$$f_{ok} = \frac{8\pi^2 m}{3e^2 h}\,\nu_{ko} \left| \epsilon_{ok} \right|^2 \qquad (4)$$

h = Planck's constant.

ϵ_{ok} is the transition dipole moment, also named electric transition moment. It can be calculated if the wave functions of the ground state and of the k'th excited state are known with sufficient accuracy. It is one of the quantities of primary importance to our purpose.

Formula (3) is an approximation since in liquid solutions, to which most of the measurements pertain, discrete absorption lines become broad continuous bands. Besides, the Lorentz-Lorenz formula for the inner field is used in this derivation. The Kramers-Kronig relations, instead, are of general applicability. In view of their later use a short discussion will be given.

If a light wave traversing a piece of matter in the x-direction can be described by

$$A.e^{-\frac{1}{2}\alpha x}e^{2\pi i\nu(t-\frac{n}{c}x)} \tag{5}$$

where A is the amplitude vector, α an absorption coefficient, ν the frequency of the light and $\frac{c}{n}$ its velocity,
the Kramers-Kronig relations can be written as

$$\begin{aligned} n(\nu) - 1 &= \frac{c}{4\pi^2}\int_{-\infty}^{+\infty}\frac{\alpha(\tau)}{\tau(\tau-\nu)}d\tau \\ \text{and } \alpha(\nu) &= -\frac{4\nu}{c}\int_{-\infty}^{+\infty}\frac{n(\tau)-1}{\tau-\nu}d\tau \end{aligned} \tag{6}$$

If the light is circularly polarized the amplitude A is complex with a component A in the y-direction and ± iA in the z-direction. The + sign corresponds to lefthanded, the - sign to righthanded polarized light. Accordingly one has to distinguish the absorption coefficients and refractive indices α_1, n_1 and α_d, n_d. From inspection of formula (5) one derives that $\alpha_1(\nu) = \alpha_d(-\nu)$. Relating the circular dichroism introduced in (2)

$$\theta(\nu) = \frac{1}{4}\{\alpha_1(\nu) - \alpha_d(\nu)\} \tag{2}$$

one sees that

$$\theta(\nu) = -\theta(-\nu) \tag{7}$$

With these assessments it becomes possible to convert the relations (6) into similar relations for the angle of rotation $\phi(\nu)$ from (1) and the circular dichroism $\theta(\nu)$, at the same time changing the integration interval from $-\infty \longrightarrow +\infty$ into an interval from $0 \longrightarrow \infty$.
The result is

$$\theta(\nu) = -\frac{2}{\pi}\int_{0}^{\infty}\frac{\nu\phi(\tau)}{\tau^2-\nu^2}d\tau \tag{8a}$$

$$\phi(\nu) = \frac{2}{\pi}\int_{0}^{\infty}\frac{\tau\theta(\tau)}{\tau^2-\nu^2}d\tau \tag{8b}$$

These relations are especially interesting if in the absorption and consequently in the dichroism as function of frequency definite bands can be distinghuished. These in turn may be supposed to be correlated with electronic transitions as also occur in the dispersion formula (3). In these cases the integrated value of the circular dichroism over the band correlated with a transition 0 ⟶ k may be used as an experimental estimate of the rotational strength:

$$R_k = \frac{3hc}{8\pi^3 N_1} \int_k \frac{\theta(\nu)}{\nu} d\nu \qquad (9)$$

This definition is similar to that of the dipole strength:

$$D_k = \frac{3hc}{8\pi^3 N_1} \int_k \frac{k(\nu)}{\nu} d\nu \simeq \frac{3e^2 h . f_{ok}}{8\pi^2 m\, \nu_{ko}} \qquad (10)$$

$k(\nu) = \frac{1}{2} \{\alpha_l(\nu) + \alpha_d(\nu)\}$, is the mean absorption coefficient as measured in unpolarized light.

From quantummechanical theory it follows that

$$R_k = \mathrm{Im}\,(\vec{\epsilon}_{ok}, \vec{\mu}_{ko}) = |\epsilon_{ok}|\,|\mu_{ko}| \cos\alpha \qquad (11)$$

just as $D_k = (\vec{\epsilon}_{ok}, \vec{\epsilon}_{ko}) = |\epsilon_{ok}|^2$ (12)

where μ_{ok} is the magnetic transition moment and α is the angle between the electric and magnetic transition moment.

It would have been more proper to add factors f(n) in the formulae (9) and (10), when converting phenomenological coefficients into quantities which should be characteristic for isolated molecules. These factors, however, are rather uncertain and are not likely to affect our final result appreciably.

From measurements of absorption and of circular dichroism or rotatory dispersion due to an optically active absorption band we thus learn the magnitude of two quantities characteristic for the underlying transition: the electric transition moment and the component of the magnetic transition moment in the direction of the electric transition moment.

These two quantities may be used as a check on our ideas about the geometry and molecular structure of optically active compounds.

We have applied this method to an optically active ketone, the β-hydrindanone, and to a number of steroids where the optically active transition of longest wavelength could be located in a diene system.

In each case the rotational strength, as derived from experiment, agrees with that calculated theoretically as to the order of magnitude. There remain, however, discrepancies which require further investigation, before their importance can be judged.

In the next chapter, we give some general theoretical considerations which will be used in the discussion of special cases.

The measuring apparatus and some particulars about its performance are described in the last chapter.

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CHAPTER II

THEORETICAL CONSIDERATIONS.

Part A. Historical.

The first attempt to correlate optical rotatory power to molecular structure on the basis of an electron theory was made by Drude ¹⁾. He assumed the presence of helical orbits along which elastically bound electrons could move under the influence of incident light. The symmetry of a helix guarantees the occurrence of optical rotation. It also makes clear that the rotational strength is proportional to the scalar product of the electric and magnetic transition moment. The motion along a helix is the superposition of a translation parallel to the axis of the helix and a circular motion in a plane perpendicular to the axis. To the first motion corresponds a changing electric moment, to the second a magnetic moment in the direction of the axis. During oscillation both moments are always in the same direction for a righthanded helix (rotational strength positive) or in opposite directions for a lefthanded helix (negative rotational strength). Qualitatively such a molecular model explains the relevant features of optical rotatory power.

A different approach was started by Oseen ²⁾ and by Born ³⁾ and later extensively used by Kuhn ⁴⁾. Their molecular model comprised parts with anisotropic polarizabilities and interactions, either non-specified or from dipole forces. The oscillating dipoles induced in the polarizable component groups by the light wave and by the mutual interactions between the groups are equivalent to a resultant electric and magnetic moment at the centre of the molecule if the geometrical arrangement of the groups allows the appearance of optical rotation. The phase relations between the electric fields acting on the differently located groups assure the sign of the scalar product of the electric and magnetic moment.

A generally valid quantummechanical formula of the rotation outside regions of absorption was derived by Rosenfeld [5] for a dilute gas. If in a liquid molecular interactions can be described with sufficient accuracy by a function of the refractive index, the quantummechanical formula becomes:

$$[\phi] = \frac{96\pi N}{hc} f(n) \sum_k \frac{\nu_k^2}{\nu_k^2 - \nu^2} \operatorname{Im} (\vec{\epsilon}_{ok}, \vec{\mu}_{ko}) \tag{1}$$

The transition moments are defined as

$$\vec{\epsilon}_{ok} = \langle \Phi_o | \vec{\epsilon} | \Phi_k \rangle; \qquad \vec{\mu}_{ok} = \langle \Phi_o | \vec{\mu} | \Phi_k \rangle \tag{2}$$

Φ_o and Φ_k are the wavefunctions for ground state and k'th excited state. The electric moment operator and the magnetic moment operator are given by:

$$\vec{\epsilon} = \sum_i e_i r_i \tag{3}$$

$$\text{and } \vec{\mu} = \sum_i \frac{e_i}{2m_i c} r_i x p_i = \sum_i \frac{e_i h}{4\pi i m_i c} r_i x \nabla_i \tag{4}$$

e_i and m_i are charge and mass of the i'th particle.

If a transition $o \longrightarrow k$ from the ground state to the k'th excited state can be described as an one-electron excitation, the corresponding term in (1) becomes the quantummechanical counterpart of the Drude theory. This mechanism has been extensively discussed by Condon et al. [6]. It has also been applied to the C=O group in optically active ketones by Kauzmann et al. [7].

Kirkwood [8] showed that application of the general formula (1) to a molecule composed of separate groups with dipole-dipole interaction leads to a result similar to the Born theory in addition to terms which arise from intrinsic rotatory power of the separate groups. In applying this theory to various molecules, its outcome was not alltogether convincing. However, as Looyenga [9] showed with several examples, if this theory is applied to molecular systems of more or less rigid conformation, a calculation of the rotation may give satisfactory results. While

Moffitt [10)] indicated how, by affixing an optical axis to each of the separate groups, the arbitrariness of the Kirkwood-splitting can be avoided.

In the vicinity or inside an absorption band which contributes to the rotatory power the Born theory is out of place and a direct calculation of transition moments is indicated as in Condon's one-electron theory. In the next part of this chapter we will combine this theory with the current molecular orbital description of the ground state and excited states of organic molecules.

Part B. Molecular Orbital treatment; one electron transition moments.

In the molecular orbital approximation the wave functions Φ_o and Φ_k are constructed from products of one electron functions ψ_i, which, after multiplication into appropriate spin functions, can be antisymmetrized. This - important as it is for energy calculations - does not need to concern us for the calculation of transition moments.

Writing the ground state as

$$\Phi_o = (\psi_1)^2(\psi_2)^2 \text{-------} \psi_n(j)\psi_n(k)$$

and as an example of an excited singlet state

$$\Phi_1 = (\psi_1)^2(\psi_2)^2 \text{------} (\psi_{n-1})^2\{\psi_n(j)\psi_{n+1}(k) + \psi_{n+1}(j)\psi_n(k)\}\frac{1}{\sqrt{2}}$$

it is obvious that the orthogonality of the molecular orbitals ψ leads to

$$\vec{\epsilon}_{01} = \langle\Phi_o|\Sigma e_i r_i|\Phi_1\rangle = \frac{1}{\sqrt{2}}\{\langle\psi_n(j)|e_j r_j|\psi_{n+1}(j)\rangle + \langle\psi_n(k)|e_k r_k|\psi_{n+1}(k)\rangle\} = \sqrt{2}\langle\psi_n|er|\psi_{n+1}\rangle \qquad (5)$$

The same applies to the magnetic moment so that, apart from the factor $\sqrt{2}$, only one electron transition moments need be considered.

In the current definitions of electric and magnetic moments these quantities are not formulated on an equal footing. This may be set right by the equivalent formulation

$$\langle\psi_k|e\,r|\psi_l\rangle = -\frac{eh}{4\pi^2 m\nu_{kl}}\langle\psi_k|\nabla|\psi_l\rangle = -\frac{ie}{2\pi m\nu_{kl}}\langle\psi_k|p|\psi_l\rangle \qquad (6)$$

where $h\nu_{kl}=E_k - E_l$. This equality holds if ψ_k and ψ_l are exact eigenfunctions of a Hamiltonian with the eigenvalues E_k and E_l. Molecular orbitals, however, are usually approximations to exact solutions of a Schrödinger equation. Therefore the expressions (6) are then not equivalent. Since in checking the results of theoretical calculations of the rotational strength with the experimental result one has to compare the electric and the magnetic transition moment, it is important to make it probable that the approximation inherent in the wave functions will affect both transition moments in the same way. Moreover the expression for the electric transition moment involving the nabla (∇) operator is of some advantage in reducing the formula for the rotational strength. If the molecular orbitals are written as linear combinations, the necessary transition moments can be dealt with along concordant lines and a splitting in partial moments results. This splitting in partial moments may be fortuitous, but anyhow, a real physical significance may certainly be attached to this result in case the molecular orbitals represent a system of separated groups with some loose coupling between them. Such a system - interesting as it might be - will not be elaborated by us now and we will restrict ourselves to molecular orbitals that are linear combinations of atomic orbitals.

Part C. L.C.A.O. formulation of transition moments.

With the definition (6) of the transition dipole moment both the electric and the magnetic transition moments can be reduced to simple combinations of bond (transition) moments if the molecular orbitals are written as linear combinations of atomic orbitals.

Substituting

$$\psi_k = \Sigma\, c_{k\alpha}\phi_\alpha \quad \text{and} \quad \psi_l = \Sigma\, c_{l\alpha}\phi_\alpha$$

the mechanical transition moments P_{kl} and M_{kl} become

$$P_{kl} = \langle\psi_k|p|\psi_l\rangle = \Sigma\, c_{k\alpha}c_{l\beta}\langle\phi_\alpha|p|\phi_\beta\rangle \qquad (7)$$

and similarly

$$M_{kl} = \langle\psi_k|r \times p|\psi_l\rangle = \sum c_{k\alpha}c_{l\beta}\langle\phi_\alpha|r \times p|\phi_\beta\rangle \qquad (8)$$

Also using the abbreviations

$$p_{\alpha\beta} = \langle\phi_\alpha|p|\phi_\beta\rangle \quad \text{and} \quad m_{\alpha\beta} = \langle\phi_\alpha|r \times p|\phi_\beta\rangle$$

we find since both operators are purely imaginary

$$p_{\alpha\beta} = -\,p_{\beta\alpha} \quad \text{and} \quad m_{\alpha\beta} = -\,m_{\beta\alpha}$$

From this follows that if the atomic orbitals ϕ are real, as is usually the case,

$$p_{\alpha\alpha} = 0 \quad \text{and} \quad m_{\alpha\alpha} = 0$$

Consequently

$$P_{kl} = \sum_{\alpha<\beta}(c_{k\alpha}c_{l\beta} - c_{k\beta}c_{l\alpha})\,p_{\alpha\beta} \qquad (9)$$

$$\text{and } M_{kl} = \sum_{\alpha<\beta}(c_{k\alpha}c_{l\beta} - c_{k\beta}c_{l\alpha})\,m_{\alpha\beta} \qquad (10)$$

Thus the evaluation of the transition moments is reduced to the evaluation of bond moments pertaining to pairs of atoms and corresponding to transitions from one atom to the other.

In analogy to the definition of bond order used in molecular orbital energy calculations we define the transitional bond orders

$$c^{kl}_{\alpha\beta} = c_{k\alpha}c_{l\beta} - c_{k\beta}c_{l\alpha} \qquad (11)$$

The electric bond moment which follows from $p_{\alpha\beta}$ is independent of the choice of the origin. The magnetic bond moment, however, as it is found from $m_{\alpha\beta}$ does depend on the choice of the origin. Therefore this point requires some discussion.

If $a_{\alpha\beta}$ indicates the position of the midpoint between the centres α and β, while r_0 locates an arbitrary point with respect to this midpoint

$$r = r_o + a_{\alpha\beta}$$

$$\text{and } m_{\alpha\beta} = \langle\phi_\alpha | r \times p | \phi_\beta\rangle = \langle\phi_\alpha | r_o \times p | \phi_\beta\rangle +$$

$$+ \langle\phi_\alpha | a_{\alpha\beta} \times p | \phi_\beta\rangle = m^o_{\alpha\beta} + a_{\alpha\beta} \times p_{\alpha\beta} \qquad (12)$$

From this formula follows that $m_{\alpha\beta} = m^o_{\alpha\beta}$ for any origin on the line parallel to the direction of $p_{\alpha\beta}$ and through the midpoint between the centres α and β. If $m^o_{\alpha\beta}$ attains a minimum value, it may be called the intrinsic moment of the "bond" between α and β, while the line parallel to $p_{\alpha\beta}$ and through the midpoint of the centres α and β will be the optical axis of the two atoms α and β 10).

The molecular transition moments expressed in the bond moments and the transitional bond orders are

$$P_{kl} = - P_{lk} = \sum_{\alpha<\beta} c^{kl}_{\alpha\beta} p_{\alpha\beta} \qquad (13)$$

$$M_{kl} = - M_{lk} = \sum_{\alpha<\beta} c^{kl}_{\alpha\beta} (m^o_{\alpha\beta} + a_{\alpha\beta} \times p_{\alpha\beta}) \qquad (14)$$

For the rotational strength of a transition from the ground state towards an excited state i, whereby an electron changes from a two-fold occupied orbital ψ_k to an orbital ψ_l, we find:

$$R_i = \mathrm{Im}\,(\vec{\epsilon}_{oi}, \vec{\mu}_{io}) = 2\,\mathrm{Im}\,(\vec{\epsilon}_{kl}, \vec{\mu}_{lk}) =$$

$$= - \frac{e^2}{2\pi m^2 c \nu_{kl}} (P_{kl}, M_{lk}) \qquad (15)$$

where the scalar product

$$(P_{kl}, M_{lk}) = \sum_{\alpha<\beta} (c^{kl}_{\alpha\beta})^2 (p_{\alpha\beta}, m^o_{\alpha\beta}) + \qquad (16)$$

$$+ \sum_{\alpha<\beta} \sum_{\lambda<\mu} c^{kl}_{\alpha\beta} c^{kl}_{\lambda\mu} (p_{\alpha\beta}, m^o_{\lambda\mu}) + (a_{\alpha\beta}, p_{\lambda\mu} \times p_{\alpha\beta})$$

$$\lambda \neq \alpha \text{ or } \beta \neq \mu$$

This splitting of the rotational strength in three parts is formally equivalent to the result of Kirkwood's considerations. Indeed, in both cases it is a consequence of writing the wavefunctions involved as sums of wavefunctions more or less localized in separate groups, in our case groups of two atoms. The groups may have atoms in common.

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CHAPTER III

OPTICAL ROTATORY POWER IN π ELECTRON SYSTEMS.

1. Introduction.

From measurements of optical rotatory dispersion of a number of compounds containing a homonuclear diene system in a six-membered ring [*], we concluded to the optical activity of their common transition at 280 mμ [1]. The ultra-violet absorption at this wavelength is generally assigned to the $\pi_1 \rightarrow \pi_1^*$ transition. Therefore transitions which are located in the π electron system may give rise to optical activity.

Guided by these observations, we have developed a model of optical rotatory power in conjugated systems. This model is applicable to polyenes, aromatics, unsatured ketones etc.. Changes in the π electron system due to deformations of the molecular frame are assumed to be mainly responsible for the encountered optical activity. Asymmetric induction may also lead to optical activity. However, it will not be dealt with in this chapter.

In the compounds measured, the diene system forms a part of a non-planar ring which either is held in a fixed position, or is present in a preferred conformation. The tendency towards even distribution of strain in the ring will bring about non-planarity of the diene system. As an example of the general model, rotational strength of the first electronic transition $\pi_1 \rightarrow \pi_1^*$ in deformed cis-butadiene is calculated. This hypothetic system may be regarded as an idealization of the asymmetric diene system in the compounds investigated.

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[*] These measurements resulted from collaboration with the vitamine D group of the organic chemical laboratory, especially with R.J. de Kock, R. van Moorselaar and J. Pot. I am particularly indebted to H.J.C. Jacobs for his help with the measurements and their theoretical elaboration.

According to the principles formulated in chapter II, the description of π molecular orbitals as linear combinations of atomic orbitals allows of a splitting of electric and magnetic transition moments in transitional bond moments between pairs of atoms.

The geometrical deformation of the conjugated system enters our calculation only by changing the relative directions of the 2p atomic orbitals. Changes in hybridization which might also contribute to the final result are disregarded although this is not based on a calculation of their magnitude.

For the diene system a formula has been derived which enables to estimate the rotational strength of its transition at 280 mμ from an inspection of the geometry of the conjugated system. The outcome of this formula will be compared with some of the experimental material available.

2. Optical activity resulting from deformations.

In general π electron systems are not optically active. As a rule stable configurations of conjugated systems are planar and the plane of the molecule is a plane of symmetry. The occurrence of a plane of symmetry makes image and mirror-image of the molecule identical and optical antipodes will not exist.

It goes without saying that the same conclusion can be drawn from the general formula given in chapter II. Still we give the calculation to bring out clearly where the symmetry comes in and why some form of deformation of the π electron system becomes necessary.

In the L.C.A.O. treatment given in chapter II C expressions for the electric and magnetic transition moments are derived. These are found proportional to:

$$P_{ij} = \sum_{\alpha<\beta} c^{ij}_{\alpha\beta} p_{\alpha\beta} \qquad (1)$$

$$M_{ji} = - \sum_{\alpha<\beta} c^{ij}_{\alpha\beta} \left(m^{o}_{\alpha\beta} + a'_{\alpha\beta} \times p_{\alpha\beta} \right) \qquad (2)$$

In the case of planar π electron systems the 2p atomic orbitals from which the bond moments $p_{\alpha\beta}$ and $m^{o}_{\alpha\beta}$ are determined have their axes of quantization perpendicular to the molecular plane. This implies that $p_{\alpha\beta}$ is directed along the bond A—B, while $m^{o}_{\alpha\beta}$ is zero. The transition moments P_{ij} and M_{ji} both are found as weighted sums of bond moments $p_{\alpha\beta}$. If M_{ji} is estimated with respect to an origin in the molecular plane the vectors $a'_{\alpha\beta}$ are parallel to this plane. Therefore M_{ji} is directed perpendicular whereas P_{ij} is parallel to the molecular plane. The partial rotational strength R_{ij} as proportional to the scalar product $P_{ij} . M_{ji}$ will be equal to zero.

We will now discuss the non-planar model. The hybridization at each atom is assumed to remain unchanged. So the non-planarity arising from strain results in a twist of the molecular frame around bonds between atoms that are nearest neighbours.

Each of these twisting deformations may manifest itself in three ways in the formulae for the electric and magnetic transition moments. First there always is a change in the bond moments $p_{\alpha\beta}$ and $m^{o}_{\alpha\beta}$. Secondly the geometry of the molecular frame affects the direction vectors $a'_{\alpha\beta}$. Moreover the coefficients of the L.C.A.O.M.O.'s which determine the $c^{ij}_{\alpha\beta}$ depend on the geometry too. A non-zero value of the partial rotational strength R_{ij} can be expected.

3. Calculation of bond moments $p_{\alpha\beta}$ and $m^{o}_{\alpha\beta}$.

The bond moments $p_{\alpha\beta}$ and $m^{o}_{\alpha\beta}$ are given by:

$$p_{\alpha\beta} = < \phi_{\alpha} | p | \phi_{\beta} > = \frac{h}{2\pi i} < \phi_{\alpha} | \nabla | \phi_{\beta} > \qquad (3)$$

$$m^{o}_{\alpha\beta} = < \phi_{\alpha} | r \times p | \phi_{\beta} > = \frac{h}{2\pi i} < \phi_{\alpha} | r \times \nabla | \phi_{\beta} > \qquad (4)$$

$p_{\alpha\beta}$ is invariant with origin; $m^{o}_{\alpha\beta}$ is evaluated with respect to a point on the line joining the nuclei A and B (cf. chapter II C).

The orbitals ϕ_{α}, ϕ_{β} etc. will be chosen as Slater functions which in local coordinate systems with their origins at A, B etc. are:

$$\phi_{\alpha} = N_{\alpha} x_{\alpha} e^{-q_{\alpha} r_{\alpha}} \qquad \text{with } N_{\alpha}^{2} = \frac{q_{\alpha}^{5}}{\pi} \text{ etc.} \qquad (5)$$

Here the x_{α}-axis is the axis of quantization of the 2p orbital ϕ_{α}.

If we restrict ourselves to considering nearest neighbours, the x-axes are both perpendicular to the line joining the nuclei A and B. Their relative orientation depends on the angle of twist δ.

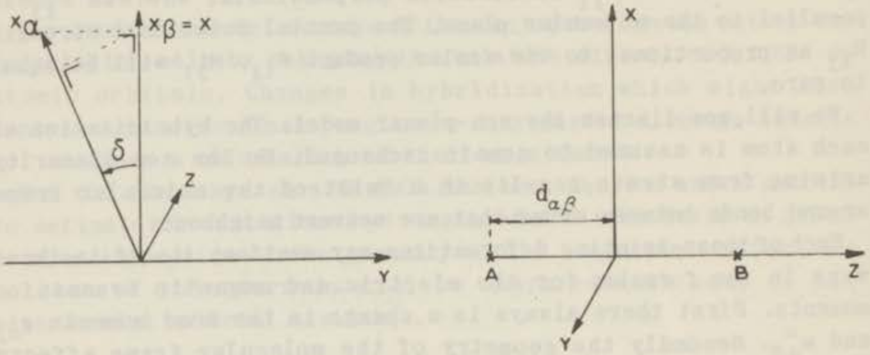


Figure 1.

It is convenient to express the orbitals ϕ_α and ϕ_β in one coordinate system with its origin at the midpoint between the nuclei A and B and parallel to the local coordinates β, with the z-axis pointing from A towards B. We will consistently use right-handed cartesian coordinate systems. The angle of twist δ will be counted positive when the x_α-axis is rotated in the direction of the minus y_α-axis.

The atomic orbitals become:

$$\phi_\alpha = N_\alpha \, (x \cos \delta - y \sin \delta) \, e^{-q_\alpha r_\alpha}$$

$$\phi_\beta = N_\beta \, x \, e^{-q_\beta r_\beta}$$

$$r_\alpha^2 = x^2 + y^2 + (z+d_{\alpha\beta})^2$$

$$r_\beta^2 = x^2 + y^2 + (z-d_{\alpha\beta})^2$$

$2d_{\alpha\beta}$ is the distance between the nuclei A and B.

With the abbreviation

$$\phi_\alpha = \alpha_x \cos \delta - \alpha_y \sin \delta$$

$$\phi_\beta = \beta_x$$

the relevant integrals become:

$$<\phi_\alpha|\nabla|\phi_\beta> = <\alpha_x|\nabla|\beta_x> \cos\delta - <\alpha_y|\nabla|\beta_x> \sin\delta$$

and $<\phi_\alpha|r \times \nabla|\phi_\beta> = <\alpha_x|r \times \nabla|\beta_x> \cos\delta - <\alpha_y|r \times \nabla|\beta_x> \sin\delta$

From symmetry considerations it is clear that only integrals

$$<\alpha_x|\frac{d}{dz}|\beta_x>$$

and $<\alpha_y|x\frac{d}{dy} - y\frac{d}{dx}|\beta_x>$ differ from zero.

Both bond moments therefore are directed along the z-axis and are proportional to cos δ and sin δ respectively.

For a further reduction of the integrals we consider:

$$\frac{d}{dz}|\beta_x> = -N_\beta q_\beta x \frac{(z-d_{\alpha\beta})}{r_\beta} e^{-q_\beta r_\beta}$$

and $<\alpha_x|\frac{d}{dz}|\beta_x> = -N_\alpha N_\beta q_\beta \int \frac{x^2(z-d_{\alpha\beta})}{r_\beta} e^{-(q_\alpha r_\alpha + q_\beta r_\beta)} d\tau$

If $q_\alpha = q_\beta = q$ (as applies to a hydrocarbon)

$$\int \frac{x^2 z}{r_\beta} e^{-q(r_\alpha + r_\beta)} d\tau = 0$$

as follows from symmetry.

By calling

$$N^2 \int \frac{x^2}{r_\beta} e^{-q(r_\alpha + r_\beta)} d\tau = Q_{\alpha\beta}$$

we may write:

$$p_{\alpha\beta} = \frac{h}{2\pi i} <\phi_\alpha|\nabla|\phi_\beta> = \frac{h}{2\pi i} q\, d_{\alpha\beta}\, Q_{\alpha\beta} \cos\delta\; s_{\alpha\beta} \qquad (6)$$

(Here $s_{\alpha\beta}$ is a unit vector pointing from nucleus A towards nucleus B).

Considering the integrals in the magnetic transition moment, we find:

$$(x\frac{d}{dy} - y\frac{d}{dx}) \mid \beta_x > = - \beta_y$$

and $< \alpha_y \mid x\frac{d}{dy} - y\frac{d}{dx} \mid \beta_x > = - S_{\alpha\beta}$

where $S_{\alpha\beta} = < \alpha_y \mid \beta_y >$ is the usual abbreviation for the overlap integral.

$$\text{Thus } m^o_{\alpha\beta} = \frac{h}{2\pi i} < \phi_\alpha \mid r \times \nabla \mid \phi_\beta > = \frac{h}{2\pi i} S_{\alpha\beta} \sin \delta \, s_{\alpha\beta} \qquad (7)$$

Moments $p_{\alpha\beta}$ and $m^o_{\alpha\beta}$ between atoms that are not nearest neighbours can be calculated along similar lines. The numerical values however are smaller. The values of the integrals Q and S decrease roughly exponentially with distance. Moreover if the axes of the 2p orbitals are not perpendicular to the line joining the nuclei as may be caused by the geometry of the molecular frame, a smaller numerical value will also result.

In order to avoid ambiguity cis and trans configurations at the double bond will be dealt with as different isomers, while the value of the angle of twist will be restricted from -90° to +90°. By an inversion of sign of δ the direction of $p_{\alpha\beta}$ is unaltered while that of $m^o_{\alpha\beta}$ reverses. So the scalar product $p_{\alpha\beta} \cdot m^o_{\alpha\beta}$, which contributes to the rotational strength R_{ij}, changes sign as is necessary with optical antipodes. Since the angle of twist δ is counted positive when the axis x_α is rotated with respect to x_β in an anti-clockwise direction as seen by an observer looking in the direction from A towards B, this choice of sign correlates a positive angle of twist with a right-handed helix along which the π electrons may move. If for a cis isomer absolute configuration is classified according to the rules of Cahn, Ingold and Prelog [2)] the prefix S corresponds to a positive angle of twist.

4. Theoretical calculation of rotational strength in diene systems.

In our model the optical activity of a diene originates from a twist of the π orbitals. The effect of twist around each of the separate bonds appears directly in the magnitude of the bond moments $p_{\alpha\beta}$ and $m^o_{\alpha\beta}$ given by (6) and (7). The electric and magnetic transition moments between one electron molecular orbitals ψ_i and ψ_j are:

$$\vec{\epsilon}_{ij} = \frac{e}{2\pi i m \nu_{ij}} P_{ij} = \frac{e}{2\pi i m \nu_{ij}} \sum_{\alpha<\beta} c^{ij}_{\alpha\beta} p_{\alpha\beta} \tag{8}$$

$$\vec{\mu}_{ji} = \frac{e}{2mc} M_{ji} = - \frac{e}{2mc} \sum_{\alpha<\beta} c^{ij}_{\alpha\beta} (m^o_{\alpha\beta} + a'_{\alpha\beta} \times p_{\alpha\beta}) \tag{9}$$

These determine the partial rotational strength of the kth transition (from the orbital ψ_i towards ψ_j).

$$R_{ij} = \mathrm{Im}\, \vec{\epsilon}_{ij} \cdot \vec{\mu}_{ji} = \frac{-e^2}{4\pi m^2 c \nu_{ji}} P_{ij} \cdot M_{ji} \tag{10}$$

also depends on the geometry of the molecular frame because of its influence on the vectors $a'_{\alpha\beta}$ and $s_{\alpha\beta}$. Finally the transitional bond orders $c^{ij}_{\alpha\beta}$ change upon alteration of the molecular frame, but we will use values from the planar model since for small angles of twist (only for these our model is applicable) these changes are of little influence on the numerical values of the bond orders c.

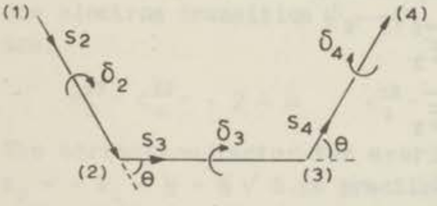


Figure 2.

We take the length of the carbon-carbon bonds $C_1 - C_2 = C_3 - C_4 = 2d_2$ and $C_2 - C_3 = 2d_3$. Therefore the integrals Q and S will be the same for the bonds $C_1 - C_2$ and $C_3 - C_4$. Angles θ between adjacent bonds are assumed to be 120° in agreement with sp^2 hybridization. Angles of twist δ_2, δ_3 and δ_4 are taken around the bonds $C_1 - C_2$, $C_2 - C_3$ and $C_3 - C_4$ respectively. The definition of sign used in the preceding § correlates a positive angle of twist with a right-handed helix (prefix S in the cis configuration).

In dealing with the geometry of the frame unit vectors s_{12}, s_{23} and s_{34} are used, pointing along the bonds from the lower numbered towards the higher numbered atom. Since only contributions from nearest neighbours will be taken into account the two suffices of these vectors prove superfluously and the first will be omitted. The same applies to other quantities. The moments p_2 and m^o_2 etc. which are directed along the bond can be written as

$p_2 = p_2\, s_2$ and $m_2^o = m_2^o\, s_2$ etc. The scalar quantities p and m are also found from (6) and (7). By choosing an arbitrary reference point, e.g. at C_3, the vectors a' towards the line joining the atoms can be taken as:

$a'_2 = -\,2\, d_3\, s_3,\ a'_3 = a'_4 = 0$

The transitional moments of the molecule become:

$$P_{ij} = c_2^{ij}\, p_2\, s_2 + c_3^{ij}\, p_3\, s_3 + c_4^{ij}\, p_4\, s_4 \qquad (11)$$

$$M_{ji} = -\, c_2^{ij}\, (m_2^o\, s_2 - 2\, d_3\, p_2\, s_3 \times s_2) + \qquad (12)$$

$$-\, c_3^{ij}\, m_3^o\, s_3 - c_4^{ij}\, m_4^o\, s_4$$

while their scalar product determines the rotational strength.

In calculating the rotational strength we have to evaluate the various vector products between unit vectors s. Some of these are different for cis and trans configurations. For both configurations we find:

$s_2 \,.\, s_3 = s_3 \,.\, s_4 = \cos\theta = \frac{1}{2}$ (13)

Further we introduce unit vectors $\vec{\xi}_2$ and $\vec{\xi}_3$ which we associate with the positive part of the 2p orbitals at C_2 and C_3. In the cis configuration these vectors may be given by:

$$s_2 \times s_3 = \sin\theta\, \vec{\xi}_2 = \tfrac{1}{2}\sqrt{3}\ \vec{\xi}_2$$

and $$s_3 \times s_4 = \sin\theta\, \vec{\xi}_3 = \tfrac{1}{2}\sqrt{3}\ \vec{\xi}_3$$

Their scalar and vector products:

$$\vec{\xi}_2 \,.\, \vec{\xi}_3 = \cos\delta_3$$

and $$\vec{\xi}_2 \times \vec{\xi}_3 = \sin\delta_3\, s_3$$

depend on the angle of twist around the $C_2 - C_3$ bond. We assume $-90^o < \delta_3 < 0^o$ and $0^o < \delta_3 < 90^o$, describing absolute configurations of opposite rotatory power. The products $s_2 \,.\, s_4$ and

$s_4 \,.\, [s_3 \times s_2]$ can be derived from:

$$s_2 = \tfrac{1}{2}\, s_3 - \tfrac{1}{2}\sqrt{3}\ [s_3 \times \vec{\xi}_2]$$

$$s_4 = \tfrac{1}{2}\, s_3 - \tfrac{1}{2}\sqrt{3}\ [s_3 \times \vec{\xi}_3]$$

We find:

$$s_2 \cdot s_4 = \tfrac{1}{4} - \tfrac{3}{4} \cos \delta_3 \tag{14}$$

$$s_4 \cdot [s_3 \times s_2] = - \tfrac{3}{4} \sin \delta_3 \tag{15}$$

In order to calculate the transitional bond orders $c^{ij}_{\alpha\beta}$ we choose the Hückel L.C.A.O. approximation. The wave functions ψ_i ordered according to the energy they belong to, are with neglect of overlap:

$$\psi_1 = \lambda \phi_1 + \mu \phi_2 + \mu \phi_3 + \lambda \phi_4$$

$$\psi_2 = \mu \phi_1 + \lambda \phi_2 - \lambda \phi_3 - \mu \phi_4$$

$$\psi_3 = \mu \phi_1 - \lambda \phi_2 - \lambda \phi_3 + \mu \phi_4$$

$$\psi_4 = \lambda \phi_1 - \mu \phi_2 + \mu \phi_3 - \lambda \phi_4$$

By solving the secular equation, we find the four roots equal to $\pm\tfrac{1}{2}\pm\tfrac{1}{2}\sqrt{5}$ and the coefficients $\lambda = 0{,}37$ and $\mu = 0{,}60$. Including overlap S the wavefunction ψ_i is to be multiplied by $(1 - x_i S)^{-\frac{1}{2}}$, where x_i is the corresponding root of the secular equation. The first electronic transition $(\pi_1 \rightarrow \pi_1{}^*)$ may be identified with the one electron transition $\psi_2 \longrightarrow \psi_3$. Its transitional bond orders c^{23} are:

$$c^{23}_2 = c^{23}_4 = - 2 \lambda \mu \qquad c^{23}_3 = - 2 \lambda^2 \tag{16}$$

The correction factor for overlap $(1 - x_2 S)^{-\frac{1}{2}}(1 - x_3 S)^{-\frac{1}{2}}$ with $x_2 = - x_3 = \tfrac{1}{2} - \tfrac{1}{2}\sqrt{5}$ is practically equal to 1.

The electric and magnetic transition moments of this transition are found equal to:

$$\vec{\epsilon}_{23} = \frac{-e}{2\pi i m \nu_{32}} [2 \lambda \mu\, p_2 \, (s_2 \cos \delta_2 + s_4 \cos \delta_4) + \\ + 2 \lambda^2 p_3 \, s_3 \cos \delta_3] \tag{17}$$

$$\vec{\mu}_{23} = - \vec{\mu}_{32} = \frac{e}{2mc} [2 \lambda \mu \{ m^o_2 \, (s_2 \sin \delta_2 + s_4 \sin \delta_4) + \\ - 2\, d_3 \, p_2 \, [s_3 \times s_2] \cos \delta_2 \} + \\ + 2 \lambda^2 m^o_3 \, s_3 \sin \delta_3] \tag{18}$$

($\vec{\mu}$ evaluated in respect of C_3.)

By scalar multiplication of (17) and (18), the rotational strength R_{23} is found and inserting (13), (14) and (15) it becomes:

$$\begin{aligned} R_{23} = \operatorname{Im} \vec{\epsilon}_{23} \cdot \vec{\mu}_{32} = \frac{-e^2}{4\pi m^2 c \nu_{32}} [& 2 \lambda^2 \mu^2 p_2 m_2^o (\sin 2 \delta_2 + \sin 2 \delta_4) + \\ & + 2 \lambda^4 p_3 m_3^o \sin 2 \delta_3 + 2 \lambda^3 \mu p_2 m_3^o (\cos \delta_2 + \cos \delta_4) \sin \delta_3 + \\ & + 2 \lambda^3 \mu p_3 m_3^o (\sin \delta_2 + \sin \delta_4) \cos \delta_3 + \\ & + \lambda^2 \mu^2 p_2 m_2^o \sin (\delta_2 + \delta_4) (1 - 3 \cos \delta_3) + \\ & + 6 \lambda^2 \mu^2 d_3 p_2^2 \cos \delta_2 \cos \delta_4 \sin \delta_3] \end{aligned} \tag{19}$$

Here the angular dependence in the bond moments and that caused by the general geometry is brought up explicitly.
The scalars p and m^o are found from (6) and (7);

$$p_\beta = \frac{h}{2\pi i} q \, d_\beta Q_\beta \qquad \beta = 2, 3, 4$$
$$m_\beta^o = \frac{h}{2\pi i} S_\beta$$

Because of equal bond lengths $p_2 = p_4$ and $m_2^o = m_4^o$.

With numerical values:

$$2 d_2 = 1{,}36 \times 10^{-8} \qquad d_2 Q_2 = 0{,}16 \qquad S_2 = 0{,}24$$
$$2 d_3 = 1{,}48 \times 10^{-8} \qquad d_3 Q_3 = 0{,}13 \qquad S_3 = 0{,}17$$
$$q = 3{,}1 \times 10^8 \quad \nu_{32} = \frac{c}{2{,}8 \times 10^{-5}} = 1{,}05 \times 10^{15}$$
$$\lambda = 0{,}37 \qquad \lambda^2 = 0{,}14 \qquad \lambda^4 = 0{,}019$$
$$\mu = 0{,}60 \qquad \lambda \mu = 0{,}22 \qquad \lambda^3 \mu = 0{,}031$$
$$\lambda^2 \mu^2 = 0{,}049$$
$$\frac{eh}{4\pi mc} = 0{,}93 \times 10^{-20} \qquad \frac{eh}{4\pi^2 m \nu_{32}} = 0{,}84 \times 10^{-25}$$

$$\begin{aligned} R_{23} = 0{,}78 \times 10^{-39} [& 1{,}17 (\sin 2 \delta_2 + \sin 2 \delta_4) + \\ & 0{,}26 \sin 2 \delta_3 + \\ & 0{,}52 (\cos \delta_2 + \cos \delta_4) \sin \delta_3 + \\ & 0{,}60 (\sin \delta_2 + \sin \delta_4) \cos \delta_3 + \\ & 0{,}58 \sin (\delta_2 + \delta_4)(1 - 3 \cos \delta_3) + \\ & 5{,}54 \cos \delta_2 \cos \delta_4 \sin \delta_3] \end{aligned} \tag{20}$$

The contribution due to coupling between electric transition moments in skew bonds is found about 3 to 10 times larger than that from coupling between an electric and a magnetic bond moment.

For small angles of twist (20) can be approximated by:

$$R_{23} = [5,5\ \delta_3 + 1,3\ (\delta_2 + \delta_4)] \times 10^{-39} \qquad (20^a)$$

The rather cumbersome derivation in this paragraph has thus led to a formula which gives the rotational strength as a linear function of the angles of twist.

5. Experimental and discussion.

Our measurements pertained to a number of steroids or closely related substances containing a diene system in a six-membered ring. Rotatory dispersion was measured in the near ultraviolet approaching the first absorption band as close as was experimentally justified. In figure 3 the molar rotations are plotted according to Lowry ($[\phi]^{-1}$ versus λ^2).

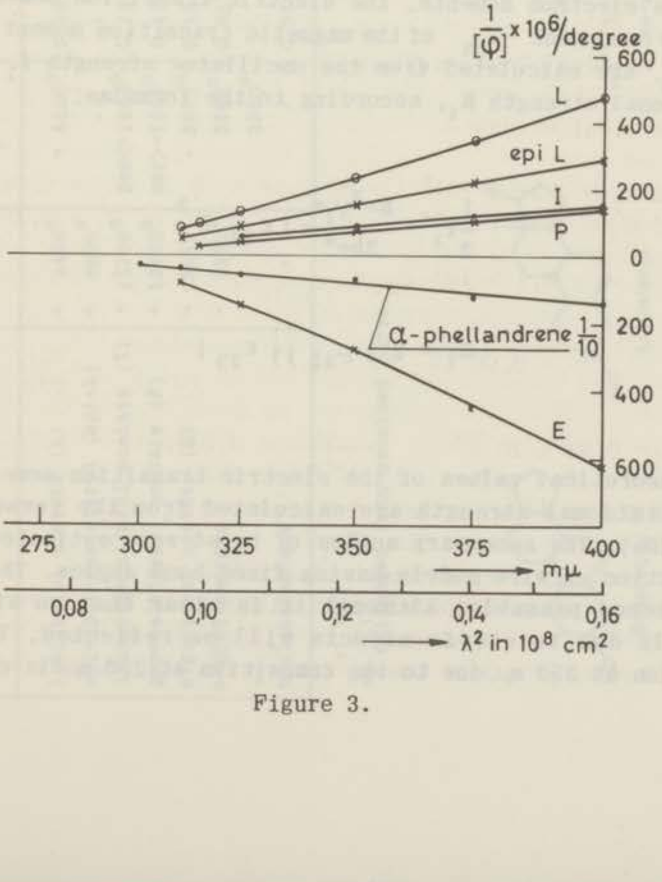


Figure 3.

Extrapolation of the linear part of these curves to zero $[\phi]^{-1}$ strongly suggests the optical activity of the transition at about 280 mμ. Assuming that the centre of the optically active band in all these compounds is located at this wavelength the rotational strength is calculated from the molar rotation at 350 mμ. This seems a reasonable procedure since this wavelength is always in the linear part of the curves and close enough to the absorption band to make the contribution of this band by far the dominating. More reliable values could have been obtained directly from the circular dichroism or by computational derivation from the rotatory dispersion measured over a large wavelength region and through the absorption band. However, measuring in the absorption band proved unfeasible with our present apparatus because of the relatively high U.V. absorption of these compounds.

In table 1 a number of quantities are collected which are important for a theoretical interpretation of the transition at about 280 mμ. The oscillator strength f_1 and the wavelength of maximum absorption is estimated from the absorption spectrum $^{3)}$, in some cases approached by a smoothed curve. The estimates are not very accurate but sufficient for our purpose. The experimental one-electron moments, the electric transition moment ϵ_{23}, and the component μ_{23} of the magnetic transition moment parallel to ϵ_{23}, are calculated from the oscillator strength f_1 and the rotational strength R_1, according to the formulae:

$$\frac{1}{2}f_1 = \frac{8\pi^2\nu_1 m}{3he^2} \mid \epsilon_{23} \mid^2 \qquad (21)$$

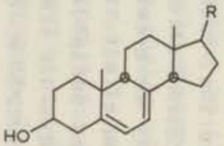
$$R_1 = 2 \mid \mu_{32} \mid \mid \epsilon_{23} \mid \qquad (22)$$

The theoretical values of the electric transition moment and of the rotational strength are calculated from the formulae (17) and (20a). The necessary angles of twist were estimated from an inspection of wire models having fixed bond angles. This procedure seems passable, although it is clear that no structural details due to steric effects will be reflected. The molar rotation at 350 mμ due to the transition at 280 mμ is calculated

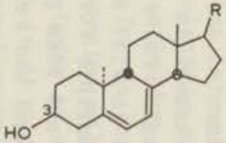
Table 1

compound	$[\phi]_{350}$ measured	$[\phi_1]_{350}$ calculated	f_{01}	λ_{max}	R_1 $x10^{39}$	ϵ_{23} $x10^{18}$ exp.	ϵ_{23} $x10^{18}$ calc.	μ_{23} $x10^{21}$ exp.	angles	
									$\delta_2=\delta_4$	δ_3
lumisterol acetate (L)	+ 4400°	+ 5500°	0,14	275 mμ *)	2,7	2,1	2,7	0,6	0	+15°
epi-(3α)-lumisterol (epi-L)	+ 6800°	,,	,,	,,	4,1	,,	,,	1,0	0	
isopyrocalciferol acetate (I)	+ 12300°	pos<+1800°	0,15	280 *)	7,5	2,2	,,	1,7	0	+5°
pyrocalciferol acetate (P)	+ 13800°	neg>-1800°	0,15	280 *)	8,4	2,2	,,	1,9	0	-5°
ergosterol acetate (E)	- 3550°	- 5500°	0,18	280 *)	2,1	2,4	,,	0,4	0	-15°
α-phellandrene	- 1300°	5500° 3200°	$0,05^5$	264	0,8	1,3	,,	0,4	0 10°	15° 0
cyclohexadiene	-	-	0,07	259	-	1,4	,,	-	-	-

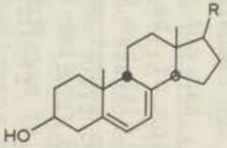
*) estimated from smoothed curve



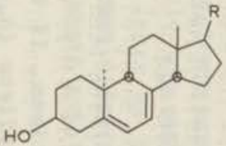
Ergosterol



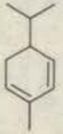
Lumisterol



Iso-pyrocalciferol



Pyrocalciferol



α - phellandrene

from the theoretical estimate of the rotational strength R_1

$$[\phi_1] = \frac{96\pi N}{hc} \frac{\omega^2}{\omega_1^{\,2} - \omega^{\,2}} R_1 \tag{23}$$

$$\text{with } \omega_1 = \frac{1}{280} \text{ and } \omega = \frac{1}{350}$$

(a possible influence of the refractive index not being considered)

The remarkable features of the longest wavelength U.V. absorption band of a diene in a six-membered ring has been considered several times. If this absorption is compared with that of trans-butadiene (λ_{max} = 220 mμ) the redshift is particularly striking. Theoretical interpretations have been reviewed by de Kock [3a)]. The transition moment which follows from the absorption intensity, has not received much attention. In a theoretical calculation of the rotatory power, however, we are mainly concerned with the transition moments. Comparing the electric transition moment as derived from the spectrum with the value calculated from our model, we find satisfactory agreement as to the order of magnitude. It is even slightly better than the one calculated according to the usual procedure (cf. Ch II). We are inclined to think that the consistent calculation of the magnetic transition moment will also yield reasonable values. In comparing the experimental and calculated values of the rotation, we find a fair agreement in some cases, in others the discrepancies are large enough to raise doubt as to the applicability of our model. Therefore we will discuss various possibilities which may be hold responsible for these discrepancies.

It does not seem probable that our estimate of the rotational strength and the related assumption of the rotation at 350 mμ being mainly due to a transition at about 280 mμ is largely at variance with the actual situation. If we had considered the rotation in the visible region of the spectrum, contributions of the Oseen-Born-Kuhn type - i.e. interaction of polarizabilities - should have been taken into account. We do not expect, however, that such an effect would be specifically due to the 280 mμ band, since the polarizability of the diene system is only slightly affected by this transition.

With a compound like α-phellandrene two conformations of the ring system with rotation of opposite sign are possible; if both these conformations are present in solution, a rotation much smaller than the one calculated can be expected. The steroids also will not always exist as rigid structures, but they may be expected to have their chromophoric system always in an identical configuration. With these compounds a comparison of calculated and measured rotations should be feasible to magnitude as well as to sign.

One might argue that the distortion of the diene system cannot be estimated from a wire model of the molecule and that one should not be amazed if angles of twist as large as 30^o or 40^o would appear in the actual molecule. This would indeed explain to a large extent the occurrence of much larger rotations than were calculated.

Table 2

$\delta_2 = \delta_4$	δ_3	R_1	$[\phi_1]_{350}$	ϵ_{23}	λ_{max}
0^o	0^o	-	-	$2{,}7 \times 10^{-18}$	220 mμ
30^o	0^o	$2{,}6 \times 10^{-39}$	4300^o	2,5	270
40^o	30^o	6,8	11000^o	2,3	270
45^o	45^o	7,8	13000^o	2,1	310

In table 2 are given the values of the electric transition moment, of the rotational strength and the rotation at 350 mμ according to (17), (20) and (23), calculated for angles of twist of about 40^o. The theoretical transition energies will also be affected when the angles of twist are of that order of magnitude. The position of the absorption band given in this table was estimated from the position of the longest wavelength absorption of planar butadiene and the transition energies in planar and in distorted butadiene both calculated according to the Hückel approximation. A possible interpretation of the observed redshift is offered by the assumption of each of the angles of twist δ_2 and δ_4 being larger than the angles δ_3.

Other difficulties remain. We mentioned the similarity in the rotatory dispersion spectra of pyro- and iso-pyrocalciferol, which are considered 9,10 syn isomers. The smaller oscillator strength of mono-cyclic dienes compared with tetracyclic ones are also not explained.

Asymmetric induction too may contribute to the rotatory power of a particular transition. With this term is meant a change of the wave functions under the influence of the electric fields of atoms etc., which do not directly participate in the chromophoric system. The 2p atomic orbitals may be modified by addition of e.g. 3p or 3d orbitals. Such an effect could be, at least partially, held responsible for the encountered optical activity of the diene system. Although the notable difference in the molar rotation of steroids with epimeric substituents at C_3, as shown e.g. by the lumisterols, may be caused by steric effects, it might equally be ascribed to an induction effect. Moreover it might as well be possible that induction should also account for variations in oscillator strength. A quantitative estimate of these induction effects, however, is rather uncertain, since practically nothing is known about the perturbations arising from the surrounding atoms.

The present experimental material is not sufficient to indicate in what respect our model is deficient or to suggest any of the complements that may be needed. Besides geometrical factors and the inductive effect one might also think of specific interactions with solvent molecules or between solute molecules due to some kind of association. This would of course invalidate the assumptions underlying our model. All this remains very speculative, however, until more experimental facts have been obtained. A larger number of substances, variation of solvent, of concentration and temperature will have to be studied.

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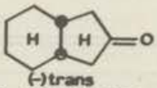
CHAPTER IV

CARBONYL COMPOUNDS.

1. Introduction.

As an example for the study of optically active C=O compounds trans β-hydrindanone has been chosen.



(-)trans
β hydrindanone

This compound has the advantage of a rigid structure, with a two-fold axis of symmetry along the C=O bond. These features will facilitate a theoretical interpretation of optical measurements in terms of molecular geometry and electronic structure. Moreover, when measuring optical rotatory dispersion and circular dichroism within the range of U.V. absorption, the high specific rotation, $[\alpha]_D = \sim 300^\circ$, will impose less stringent instrumental requirements.

Before discussing the U.V. absorption band at 290 mμ and its bearing on the optical rotatory power, it will be useful to review shortly the present ideas about the electronic structure of the C=O group [1)]. In most carbonyl compounds the bonds in which the C-atom participates are co-planar, enclosing angles of 120° (cf. figure 1). The local symmetry of the C=O group therefore is C_{2v} (two planes of symmetry and a two-fold axis). A trigonal hybridization (sp^2) of carbon is implied by this picture. The hybrid orbitals can be represented by:

$$t_1 = +\tfrac{1}{2}\sqrt{2}\,Y^C + \tfrac{1}{6}\sqrt{6}\,Z^C + \tfrac{1}{3}\sqrt{3}\,S^C$$

$$t_2 = -\tfrac{1}{2}\sqrt{2}\,Y^C + \tfrac{1}{6}\sqrt{6}\,Z^C + \tfrac{1}{3}\sqrt{3}\,S^C$$

$$t_3 = \qquad -\tfrac{1}{3}\sqrt{6}\,Z^C + \tfrac{1}{3}\sqrt{3}\,S^C$$

(Here the symbols S^C, Y^C and Z^C represent the 2s, $2p_y$ and $2p_z$ atomic orbitals at carbon.)

Of these orbitals only the one extending towards oxygen (t_3) is considered as a part of the C=O group. The other two hybrids are supposed to take part in strong localized bonds with the other two attached atoms.

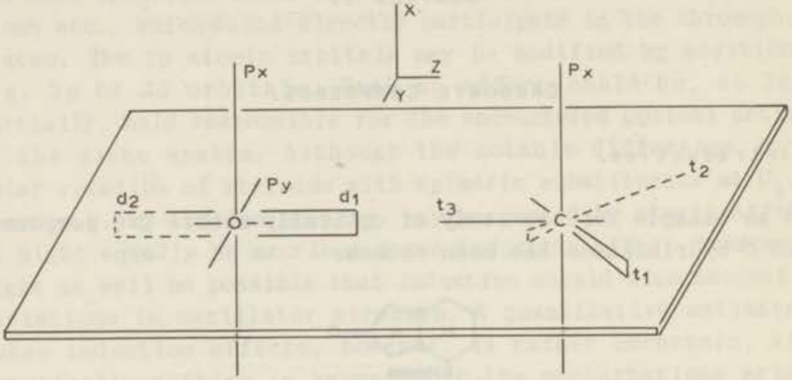


Figure 1: Orientation of the atomic orbitals in the C=O group. (The z-axis in the O-C direction along the axis of symmetry.)

Regarding the hybridization at oxygen the description is less precise. Some form of digonal hybridization can be assumed, e.g.:

$$d_1 = + c\, Z^0 + \sqrt{1 - c^2}\, S^0$$

$$d_2 = - \sqrt{1 - c^2}\, Z^0 + c\, S^0$$

with c at present not further specified.

From the hybrids and the remaining 2p orbitals of carbon and oxygen, molecular orbitals can be constructed:

$$\sigma = \lambda_\sigma d_1 + \mu_\sigma t_3 \qquad \sigma^* = \lambda'_\sigma d_1 - \mu'_\sigma t_3$$

$$\pi = \lambda_\pi X^0 + \mu_\pi X^C \qquad \pi^* = \lambda'_\pi X^0 - \mu'_\pi X^C$$

These orbitals are bonding and anti-bonding respectively. Lastly the orbitals

$$Y^0 \text{ and } d_2$$

describe non-bonding orbitals localized at oxygen.

The sequence of the orbitals according to their energies, as based upon spectroscopical evidence, is given in figure 2. Uncertainty exists as to the energy of the non-bonding orbital d_2. It is connected with the hybridization at the oxygen atom.

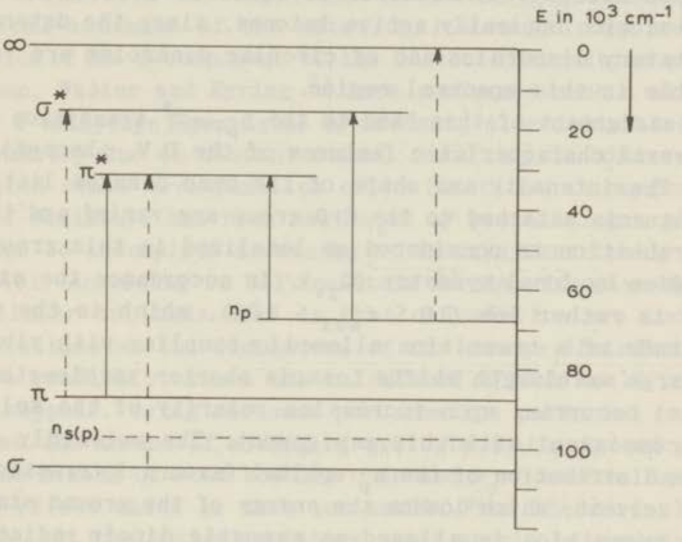


Figure 2: Term scheme of the orbitals in the C=O group.

In the ground state two electrons can be assigned to each of the four lowest orbitals. Absorption in the ultra-violet leads to the excitation of an electron from the bonding or non-bonding orbitals to one of the anti-bonding orbitals or to still higher levels. Observed absorption bands are located at 290 mμ, at about 200 mμ or possibly at somewhat shorter wavelength, near 180 mμ and near 150 mμ. Although the bands in the vacuum U.V. have been observed in only a few instances and values in this region may differ for different compounds, the general appearance of the absorption spectrum is quite similar in a variety of compounds. Ultimately, this similarity justifies the treatment of the carbonyl group as a separate chromophoric system.

The bands at wavelengths a little below 300 mμ and 200 mμ are ascribed to the transition $n_p \longrightarrow \pi^*$ and $n_p \longrightarrow \sigma^*$ resp. The band at 180 mμ probably is to be identified with the transition $\pi \longrightarrow \pi^*$. The assignment of the band at 150 mμ is not certain; transitions $\pi \longrightarrow \sigma^*$, $\sigma \longrightarrow \pi^*$ as well as a Rydberg-series have been considered. In this description transitions from the level belonging to the non-bonding orbital d_2 are generally not considered.

2a. The $n_p \longrightarrow \pi^*$ transition in absorption.

The absorption band at 290 mμ in aliphatic carbonyl compounds has been extensively studied. It is of particular interest in relation with optically active ketones, since the determination of rotatory dispersion and of circular dichroism are very well possible in this spectral region.

The assignment of this band to the $n_p \longrightarrow \pi^*$ transition is based on several characteristic features of the U.V. absorption spectrum. The intensity and shape of the band changes little, when substituents attached to the C=O group are varied and therefore the transition is considered as localized in this group. It is forbidden by local symmetry (C_{2v}). In accordance the extinction value is rather low ($10 < \epsilon_{max} < 100$), which is the order of magnitude of a transition allowed by coupling with vibrations. The large wavelength shifts towards shorter wavelengths (blue-shifts) occurring upon increasing polarity of the solvent are also consistent with this assignment. The outwardly directed charge distribution of the n_p orbital favours interaction with a polar solvent, which lowers the energy of the ground state.

The transition is allowed as magnetic dipole radiation, but the observed intensity ($f = 10^{-3}$ till 10^{-4}) is too large to be attributed to this mechanism. An oscillator strength of this order of magnitude must be ascribed to an electric dipole. An electric dipole transition which is forbidden because of symmetry (also in case of local symmetry) may become allowed if this symmetry is sufficiently lowered by a distortion of the molecule. This distortion may be due to vibrations; further, if the transition is forbidden by local symmetry only, there may be interactions with distant atoms which are large enough to affect the symmetry, so that the transition becomes allowed. In a following section we will discuss these mechanisms more fully.

2b. Optical activity in the $n_p \longrightarrow \pi^*$ transition.

Optical activity in ketones is partly due to the $n_p \longrightarrow \pi^*$ transition as follows from rotatory dispersion or more directly from circular dichroism. This may be interpreted theoretically as a simultaneous occurrence of a magnetic dipole and an electric dipole transition. The observed circular dichroism is proportional to the component of the electric transition moment in the direction of the magnetic transition moment. This magnetic moment is mainly localized at oxygen and orientated parallel to the C=O bond (z-polarized) pointing away from the carbon atom. As an allowed transition its magnitude is nearly $1\mu_{\beta}$. Therefore a theoretical estimate of the rotational strength requires the calculation of the z-component of the electric transition moment.

Kauzmann, Walter and Eyring $^{2)}$ have performed such a calculation for 3-methylcyclopentanone by assuming a deviation from the local symmetry due to distant atoms, resulting in admixture to the excited state wave function of 3d functions at oxygen. The extent of admixture has been estimated by postulating a perturbation due to incomplete screening of the (asymmetrically located) nuclei. According to Vol'kenshtein $^{3)}$ the effective charges in the Slater orbitals used in that calculation are too low; this overestimates the dimensions of the charge distributions. With more realistic values the calculated effect would practically disappear. Using the same perturbation potential he also calculates the amount of mixing of orbitals in the ground state, namely the mixing of some bonding π to the n_p function. Again he finds an effect which is much too small. From these results he concludes that the optical rotatory power should be explained by an interaction of polarizabilities of the type as discussed by Born, Oseen and Kuhn.

Although his criticism seems convincing, his suggestion as to the origin of the rotatory power does not provide an explanation of the circular dichroism of the 290 mμ band as an one-electron transition. It may be that the idea of Kauzmann c.s. as to the admixture of a 3d orbital at oxygen is supported by the octant rule $^{4)}$. For this mixing a perturbation is required proportional to the product xyz, which is just what one would expect as a basis for the octant rule. Indeed, this rule is formulated by assuming admixture of 3d functions $^{4a)}$. Moreover, quantitative agreement between calculated and experimentally estimated rotational strengths of a number of monocyclic and bicyclic ketones has been obtained by assuming the same perturbation potential and nearly identical wave functions as were used by Kauzmann c.s..

However, one might argue that Vol'kenshtein's criticism should also apply to this recent work. In this entangled situation it may be helpful to take a somewhat different point of view.

First of all, we want to point out that the absorption intensity in optically active compounds is of the same order of magnitude as is found in inactive compounds. Therefore a theory of the absorption intensity should equally apply to both groups of compounds.

Secondly, one may determine the electric transition moment from the observed absorption intensity and use this value to calculate from the rotational strength the minimum value of the magnetic transition moment. From our measurements we deduce in this way a value which seems difficult to explain as will be discussed later.

The next sections will be devoted to the discussion of these two points.

2c. Intensity calculations for $n_p \longrightarrow \pi^*$ transition.

In carbonyl compounds like formaldehyde or acetone the $n_p \longrightarrow \pi^*$ transition is forbidden in the equilibrium position of the nuclei because of the high symmetry of the molecular frame in these compounds. In less symmetrical compounds it may become allowed but the local symmetry around the carbonyl group will keep the value of the electric transition moment very low. As soon as the symmetry is lowered, due to vibrations of the molecule or to a distortion of a permanent character, the transition probability rises so that light absorption becomes measurable. The coupling of electric dipole transitions with vibrations has been treated by Herzberg and Teller 5). Murrell and Pople 6) have elaborated this method.

The dependence of the electric transition moment on the relative positions of the nuclei in a molecule can be expanded into a Taylor series:

$$\vec{\epsilon}(Q) = \vec{\epsilon}(o) + \sum Q_\xi \left(\frac{d\vec{\epsilon}}{dQ_\xi}\right)_o + \text{-----} \qquad (1)$$

Q_ξ = ξ'th normal coordinate (this determines the positions of the nuclei during the ξ'th normal vibration).

Q = shorthand notation for all the normal coordinates.

$\vec{\epsilon}(Q)$ = electric transition moment as a function of Q.

$\vec{\epsilon}(o)$ = electric transition moment with the nuclei in some reference position (o).

$\left(\frac{d\vec{\epsilon}}{dQ_\xi}\right)$ = variation of the transition moment due to the vibration described by Q_ξ.

For allowed transitions the term $\vec{\epsilon}(o)$ generally is large compared with the other terms in the expansion and the transition moment may be discussed in terms of the electronic part of the wave functions only. For symmetry forbidden transitions $\vec{\epsilon}(o) = 0$; for transitions forbidden only by local symmetry $\vec{\epsilon}(o) \neq 0$, but is comparatively small. Therefore in these cases the variations of the transition moment have be to taken into account.

Assuming for the moment $\vec{\epsilon}(o) = 0$, the absorption intensity of a separate vibronic transition from the zero'th vibrational level of the electronic ground state (0,o) towards the k'th vibrational level of the K'th excited state (K,k) becomes

$$|\epsilon_{Kk \longleftarrow 0o}(Q)|^2 = \Sigma \left(\frac{d\vec{\epsilon}}{dQ_\xi}\right)^2 < \chi_o | Q_\xi | \chi'_k > < \chi'_k | Q_\xi | \chi_o > \qquad (2)$$

where χ_o and χ'_k represent the vibrational wave function of the appropriate levels. The summation of this expression over all vibrational levels going with the excited state should yield the dipole strength of the electronic transition K⟵0.

The factors $\frac{d\vec{\epsilon}}{dQ_\xi}$ are estimated by considering the small displacements of the nuclei during the zero-point vibrations. Such a displacement results in a perturbation which is equivalent to that of a dipole at the original position of the nucleus and directed parallel to the displacement. Its magnitude is equal to the product of the effective charge of the nucleus into the root mean square displacement. In the next stage of the calculation according to the Herzberg-Teller approach each of the perturbations is evaluated by expanding the wave function in the perturbed state into a series of those of the unperturbed system. Of course the complete set of the wave functions should be used, but only those of neighbouring states are generally taken into account.

Along these lines Pople and Sidman [7]) have calculated the absorption intensity of the 290 mμ band in formaldehyde. They consider the effect of motions of the two H-atoms relative to the C=O group. The only motions which may have the desired effect are the parallel displacements of the H-atoms in the x-direction or in the y-direction. The result of their calculation is that the transition becomes allowed mainly due to the out-of-plane wagging mode of vibration. This mode (symmetric with respect to the xz-plane, therefore indicated as S_x in table 1) describes the parallel motion of the hydrogens in the x-direction, the resulting transition is mainly y-polarized.

At this point we want to raise some criticism. In the Herzberg-Teller approach the perturbations due to the nuclei affect all electrons. Pople and Sidman take into account the perturbations of the electrons in the C=O bond only, whereas the other electrons remain unaffected. According to the Born-Oppenheimer approximation these electrons would be expected to follow the motion of the nuclei. This will counterbalance the calculated dipoles to a large extent. On the other hand, in this picture there now appears a change in the hybridization at the C-atom of the C=O group as the main effect from which the observed intensity originates. Here again, the result is that the transition is mainly y-polarized.

In ketones, like acetone or cyclopentanone, the transition may also become allowed because of a kind of rocking mode (A_x) in the CH_3- or CH_2- groups, absent in formaldehyde. The symbol A_x is used to indicate that part of the motions in the x-direction which is antisymmetric with respect to the zx-plane perpendicular to the plane of the molecule; this motion is also antisymmetric with respect to the xy-plane. It destroys the symmetry of the molecule such that at most a two-fold axis remains and optically active configurations are reached. Starting from planar cyclopentanone e.g. this situation would be realized if one of the CH_2- groups adjacent to the C=O group is twisted such that its H-atoms move upwards whereas in the other CH_2- group the H-atoms move downwards. If the interaction of the CH_2- group with the electrons of the C=O group can be described as due to two dipoles, one will have the direction of the positive x-axis, the

Table 1

induced transition moment of $n_{p_y} \longrightarrow \pi^*_x$ transition

states unperturbed	 admixed	vibration	resulting polarization
π^*	σ^*	S_x	y
n_{p_y}	σ	A_y	x
n_{p_y}	π	A_x	z

other of the negative x-axis. These dipoles will produce a perturbation at the oxygen atom proportional to the product xy. As a consequence of this the n_p state will mix with some π bonding wave function giving rise to a transition with finite probability and polarized in the z-direction. The result of these considerations are summarized in table 1.

The perturbation that would bring with it a mixing of $3d_{zx}$ with n_{p_y} or of $3d_{yz}$ with π_x requires a product xyz, which is a higher term in the Taylor series of the perturbing potential and therefore presumably less important.

The question may arise why cyclopentanone e.g. which presumably has a component of the electric transition moment in the z-direction and an allowed magnetic dipole transition moment in the same direction does not show optical activity. Analogously to the formula (2) for the dipole strength the contribution of a separate vibronic transition to the rotational strength becomes:

$$r_{Kk} = \mathrm{Im}\,(\vec{\epsilon}_{Kk \longleftarrow Oo}, \vec{\mu}_{Oo \longrightarrow Kk}) \qquad (3)$$

For the magnetic transition moment only the first term $\vec{\mu}(o)$ in the Taylor expansion is of importance, whereas the electric transition moment starts with $Q_\xi (\frac{d\vec{\epsilon}}{dQ_\xi})_o$. This means that the rotational strength r_{Kk} can be written as

$$r_{Kk} = (\vec{\mu}(o) < \chi_o | \chi'_k >, \Sigma (\frac{d\vec{\epsilon}}{dQ_\xi})_o < \chi'_k | Q_\xi | \chi_o >) \qquad (4)$$

If the vibrational functions χ correspond to a parabolic or other symmetric potential function the factors in (4) cannot simultaneously differ from zero. Therefore the rotational strength will be zero.

Let us consider an optically active configuration fixed e.g. in cyclopentanone by fusing the five membered ring to a cyclohexane ring in a *trans* ring juncture, as in optically active β-hydrindanone. The potential function becomes a double-minimum function with a barrier high enough to prevent racemization by tunnelling. Now the vibrational wave functions will belong to one of the hollows in the potential corresponding to a laevo- or dextro-rotatory configuration of the molecule. These wave functions will not be symmetric or antisymmetric with respect to the zero value of Q and therefore both factors in (4) involving these functions may at the same time differ from zero.

If the symmetry of the molecule is the same as that of the chromophoric system (C_{2v}) the electric transition moment is due to vibrations only. In ketones of lower symmetry (not necessarily optically active) there may also be a moment caused by time-independent interactions with asymmetrically located atoms. The problem of evaluating the resulting transition moments remains, however, essentially the same whether one considers symmetric or asymmetric, optically active of optically inactive ketones. One would therefore expect that the mechanism which accounts for the electric transition moment of the 290 mμ band will be very similar in all these cases.

3. Experimental.

Spectra of β-hydrindanone.

Ultra-violet absorption spectra *) are reproduced in figures 3, 4 and 5; three solvents of widely differing polarity were used: methyl alcohol ($\epsilon = 25$), dioxane ($\epsilon = 4$) and isooctane ($\epsilon = 2$). A blue-shift upon increasing polarity of the solvent is not very pronounced. Striking is the difference in fine-structure which is well resolved on the long wave length side of the band in the solvent isooctane.

Optical rotatory dispersion spectra in these solvents, reproduced in figures 7, 8 and 9, show a similar feature. Again the fine-structure is better resolved in a solvent of less polar character. These spectra differ from the data of Bourn and Klyne 8), who report only one peak and one trough in all solvents used.

Circular dichroism was measured in isooctane as the solvent (figure 6). As a check **) on the measurements the circular dichroism was also calculated from the dispersion curve by application of the Kramers-Kronig relations (cf. Ch. I). That part of the rotation that was estimated to be due to bands at shorter wave length was first substracted. The resulting curve is given

*) The absorption spectra were recorded of a Cary M14 spectrophotometer. Its radiation is by far sufficiently monochromatic to resolve the observed fine-structure adequately.

**) I wish to acknowledge with gratidude the valuable assistance of Miss M.J. Wiggers de Vries in carrying out these calculations by a numerical method, which will be the subject of a future article.

in figure 11. A fair agreement between the shapes of the calculated and experimental curve was found, but the calculated values were some 15% higher than the observed ones. We are inclined to attribute these differences for the larger part to uncertainties in the measurement of the circular dichroism.

Although the absorption curve and the dichroism curve are very similar in shape the ratio of dichroism to absorption (g-factor) varies with wave length. It is possible to split up each curve into two different ones each with a constant g-factor (figures 10 and 11). The longest wave length curve shows pronounced fine-structure and the typical features of a progression due to the C=O stretching vibration. The distance between consecutive peaks is 1200 - 1210 cm^{-1}. In the, well understood, absorption spectrum of formaldehyde it is 1180 cm^{-1}, and the intensity ratios too are very similar. The other curve reveals very little fine-structure. It may be of interest that in the 290 mμ band of camphor 9) the g-factor is not constant either but here no fine-structure has been found and a splitting up of the band becomes more arbitrary.

To check the idea that the longest wave length part may be interpreted as a single progression, the relative intensities of the components of this part of the spectrum were calculated from an approximation of the C=O stretching mode. Harmonic oscillators were used as the vibrational eigenfunctions, for the ground

Table 2

relative intensities in the progression due to the C=O stretching mode

	calculated intensities (square of overlap of harmonic oscillators)					observed intensities	
	p = 1,40	1,50	1,55	1,70	2,00	at wavenumber	relative height
$0 \leftarrow 0$	1	1	1	1	0,4	30.850	1
$1 \leftarrow 0$	1,39	1,59	1,72	2,04	1	32.050	1,7
$2 \leftarrow 0$	0,72	0,98	1,14	1,74	1,25	33.250	1,2
$3 \leftarrow 0$	0,16	-	0,38	0,76	0,9	34.450	0,45
$4 \leftarrow 0$	-	-	0,04	-	0,44	35.650	0,1

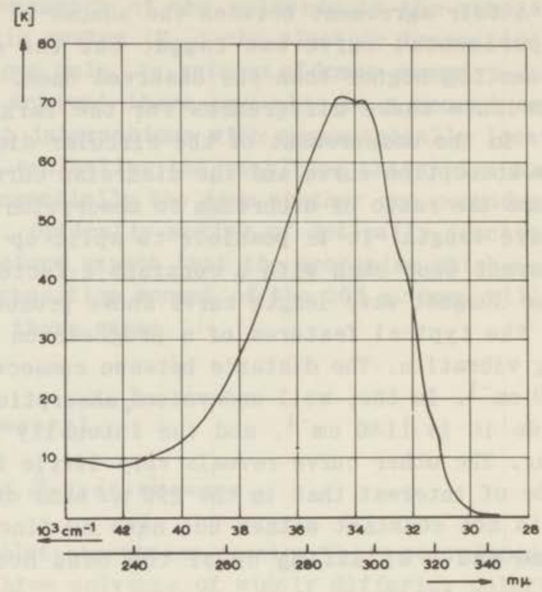


Figure 3: U.V. absorption, solvent methyl alcohol.

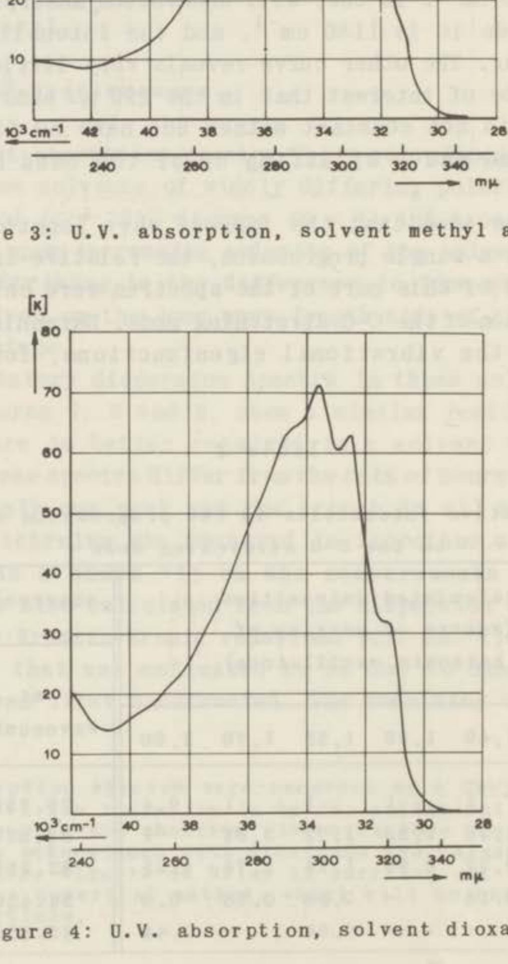


Figure 4: U.V. absorption, solvent dioxane.

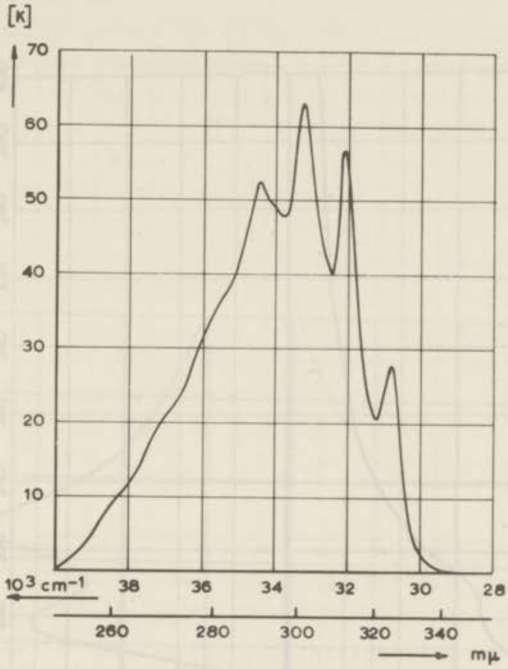


Figure 5: U.V. absorption, solvent isooctane.

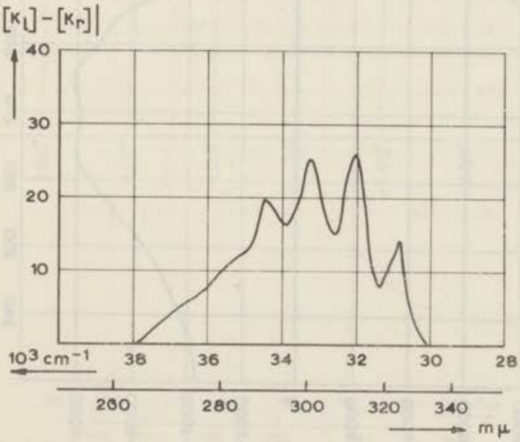


Figure 6: Circular dichroism, solvent isooctane (directly measured as the ellipticity).

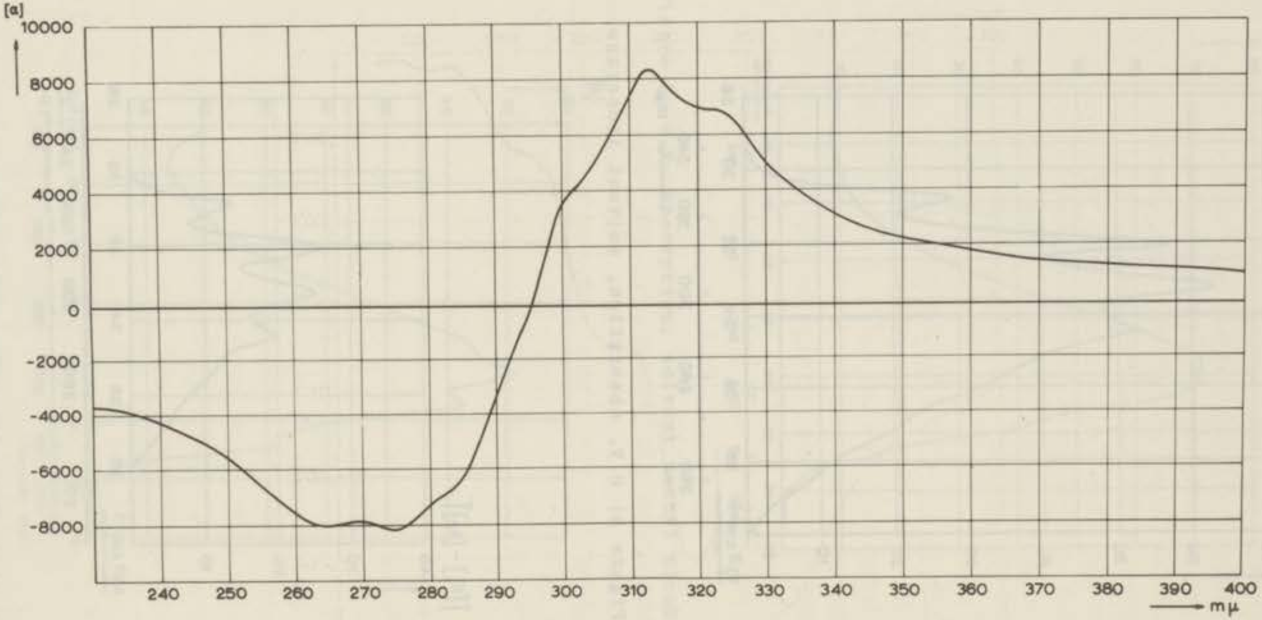


Figure 7: Rotatory dispersion, solvent methyl alcohol.

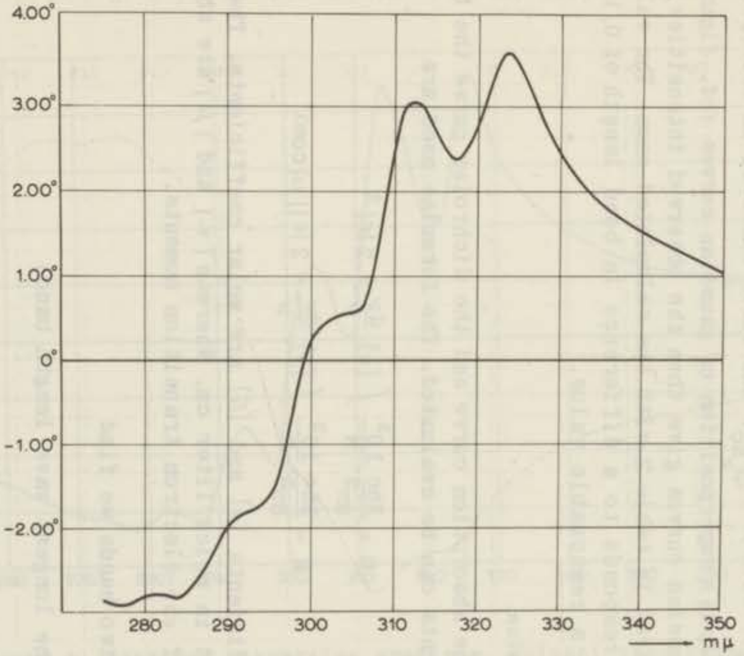


Figure 8: Rotatory dispersion spectrum of an optically impure sample (estimated purity about 90%), solvent dioxane.

state and for the excited state with different frequencies (ω_g = 1750 cm^{-1} and ω_e = 1205 cm^{-1}) and different equilibrium positions. The frequencies were taken from the infrared spectrum and from the observed U.V. absorption progression. The force constant for the ground state was taken as k_g = 10,2 x 10^5 dyne/cm $^{10)}$. With these data relative intensities were calculated in terms of a parameter $p = \sqrt{\beta}(d_g - d_e)$, proportional to the difference in equilibrium distance in the ground state (d_g) and in the excited state (d_e), with $\beta = \frac{\omega_e}{\omega_g}\frac{k_g}{hc}$. The curve observed in absorption can be built up as a superposition of gaussian curves (cf. figure 10). These gaussian curves give then the observed intensities. These are compared in table 2 with the calculated ones. The value p = 1,55 corresponds to a difference in bond length of $0,108^5$ Å, which is a reasonable value.

Discussion.

From the absorption curve and the dichroism curve the transition moments can be evaluated. The formulae used are

$$D = \frac{3hc}{8\pi^3}\cdot\frac{10^3}{N}\int [\kappa]\,\frac{d\nu}{\nu} = 2\,|\epsilon|^2$$

$$R = \frac{3hc}{8\pi^3}\cdot\frac{10^3}{N}\int [\theta]\,\frac{d\nu}{\nu} = 2\,|\epsilon|\,|\mu|\cos\alpha$$

The coefficients $[\kappa]$ and $[\theta]$ are molar coefficients. These are expressed in moles/liter cm. Whereas $|\epsilon|$ and $|\mu|$ are absolute values of *one*-electron transition moments.

For the two bands we find

A (the longest wave length band)

$D = 0,7.10^{-38}$ $\qquad \epsilon = 0,59.10^{-19}$

$R = 1,1.10^{-39}$ $\qquad \epsilon\,\mu\cos\alpha = 0,92.10^{-20}$

B (the shortest wave length band)

$D = 2,65.10^{-38}$ $\qquad \epsilon = 1,15.10^{-19}$

$R = 2,65.10^{-39}$ $\qquad \epsilon\,\mu\cos\alpha = 1,14.10^{-20}$

In both cases the values of the magnetic transition moments are higher than would be expected. The magnetic transition moment

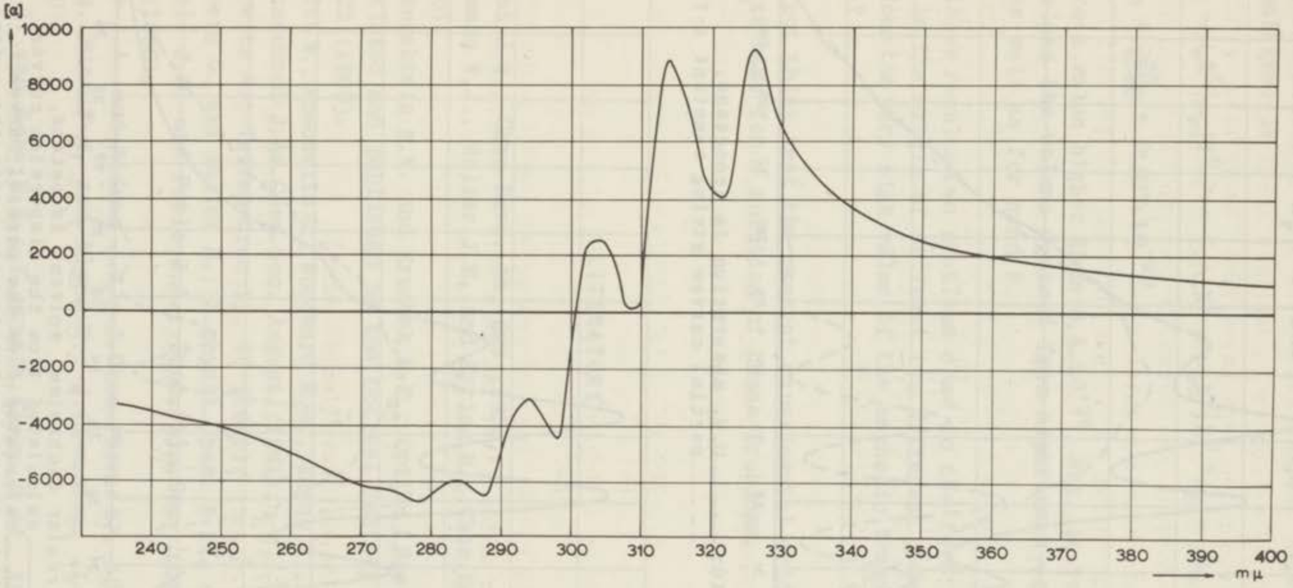


Figure 9: Rotatory dispersion spectrum, solvent isooctane.

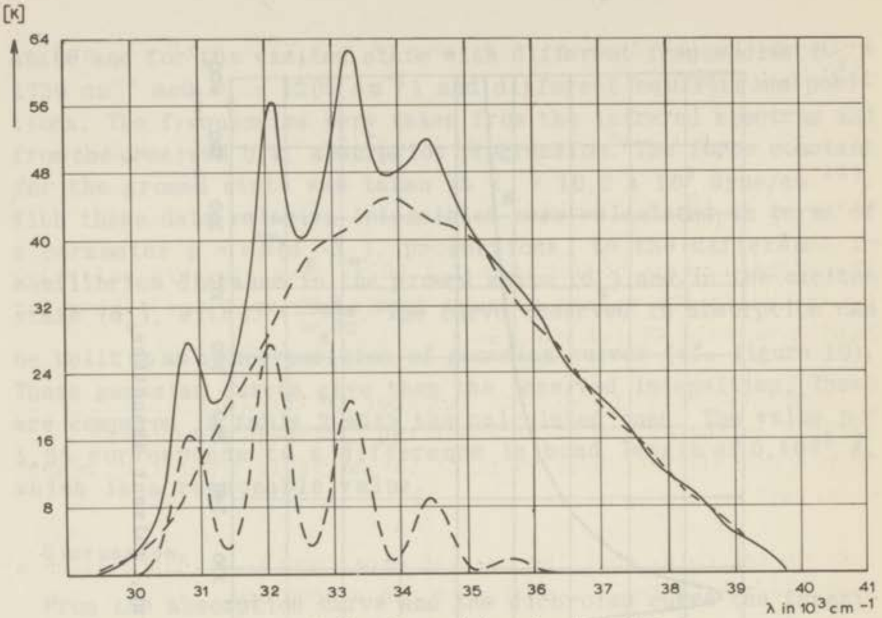


Figure 10: ——— U.V. absorption in isooctane,
– – – – partial curves giving constant g-factors.

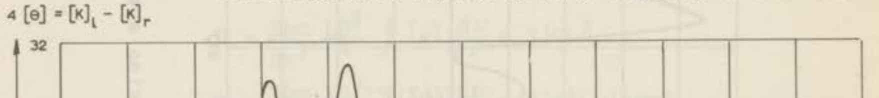


Figure 11: Circular dichroism, solvent isooctane,
——— calculated from the dispersion curves,
– – – – calculated from the partial curves
of figure 10 by multiplication with the g-factors 0,63
and 0,387.

between the orbitals $n_p = Y^0$ and $\pi^* = \lambda'_\pi X^0 - \mu'_\pi X^C$ (λ'_π and μ'_π both positive) is

$$< \lambda'_\pi X^0 - \mu'_\pi X^C | \mu_z | Y^0 > = < \lambda'_\pi X^0 - \mu'_\pi X^C | X^0 > \mu_\beta = (\lambda'_\pi - \mu'_\pi S)\mu_\beta$$

where $\mu_\beta = \frac{eh}{4\pi mc} = 0,927.10^{-20}$.

Therefore a value higher than $0,4.10^{-20}$, say, is very unlikely. Nevertheless the values deduced from experiment are higher for band A as well as for band B.

From these results two problems come to the fore:

1º What is the origin of at least two different g-factors?
2º How does the very high value of the magnetic transition moment arise?

We do not think that the present experimental evidence gives a sufficient base for a solution of these problems.

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CHAPTER V

MEASURING APPARATUS.

The measurements of rotatory dispersion and circular dichroism reported in the chapters III and IV were performed with an apparatus assembled from the following constituent parts:

A Bausch & Lomb grating monochromator (1200 grooves/mm) blazed at 300 mμ equipped with condensor lens and the standard light sources (Nester hydrogen arc, tungsten band lamp and mercury arc); two Glan polarizing prisms (Halle), the analysor fixed in a graduated circle which was equipped with a vernier readable to one minute of an arc; sample cells of 1,2 and 5 cm length with fused silica windows; a Soleil compensator (Steeg und Reuter), its retardations readable at $\frac{1}{1000}$ λ at 300 mμ; a photomultiplier tube (R.C.A., IP 28), fed with high voltage, continuously adjustable down to -1150 Volt; a mirror galvanometer (Kipp & Zonen), sensitive to 5 x 10 $^{-11}$ Amp., to indicate the photocurrent without amplification.

On an optical bench of 1 m length were mounted the polarizing prisms, sample cell holder, phototube and Soleil compensator, the latter only when measuring circular dichroism. The field (8^{o}) and the dimensions (15x15x16mm) of the polarizing prisms determined the diameter of the beam of light. To gather as much light as possible a slightly convergent beam was used with the exit of the monochromator imaged on the photomultiplier tube. As exit was used a circular diaphragm of 1 mm diameter; this filled the aperture of the polarizor and suppressed some spurious light.

The quality of performance obtained from this apparatus depended almost solely on the intensity and spectral purity of the light as determined by the monochromator. The 1 mm width of the slits corresponds to a band width of 0,3 mμ. In actual practice it was probably better than this value since a circular exit was used. Stray light from the monochromator could give rise to serious errors. For samples of high optical density the small initial fraction of stray light (about 0.5%) became considerable in the radiation finally detected. Therefore, as a rule, samples of less than unit optical density were measured. By the use of a suitable auxiliary filter, reliable measurements could be made of somewhat denser samples.

Rotation measurements were made by the method of symmetrical angles$^{1)}$. Blank readings could be made in the visible and ultra violet between 700 mμ and 220 mμ. The spectral response of the phototube limited the sensitivity in the red. Towards the low wavelength side, below 230-240 mμ the decrease in transparency of the prisms and windows lead to less reliable values. The ultimate limit depended on the nature and the purity of the solvents used. When measuring the rotation of transparent media small symmetrical angles were used (3^o to 5^o) and medium voltage applied to the phototube. The reproducibility and accuracy of the resulting measurements were then determined by the readings of the analysor displacements (possible to 1′ or 2′). Larger symmetrical angles and maximum voltage to the photomultiplier tube became necessary when measuring an absorbing sample and the reproducibility was decreased to 3′ to 5′. Moreover the accuracy was limited further under such circumstances by a systematic error due to the relatively increased amount of stray light.

Circular dichroism was measured as an ellipticity resulting from differences in absorption of the circular components of plane polarized light. By a variable wave retardation plate (Soleil compensator) orientated with its axes at 45^o towards the initial plane of polarization, the ellipticity of the sample could be compensated. By determining the photocurrent minimum with respect to variations in the settings of the analysor and the compensator the rotation and the ellipticity of the sample could be established. The small ellipticity which is caused by an optically active sample can be taken to be equal to its circular dichroism. The accuracy of the dichroism spectrum obtained in this way is comparatively small, but to attain the highest accuracy would have required corrections for almost unavoidable errors resulting from the manufacturing and mounting of the double refracting plates of the Soleil compensator$^{2)}$. Furthermore, measurements made with less than perfectly parallel light also give rise to systematic errors. However when measurements were carried out according to the method outlined, it was possible to perceive relative differences.

The above description demonstrates that it is feasible to construct a spectropolarimeter at a fraction of the cost of the commercially available ones. We realize nonetheless that the system used by us is laborious and obsolete as far as the measurement of rotation is concerned. Improved systems and new concepts have been proposed recently and are applied in instrumental design³⁾.

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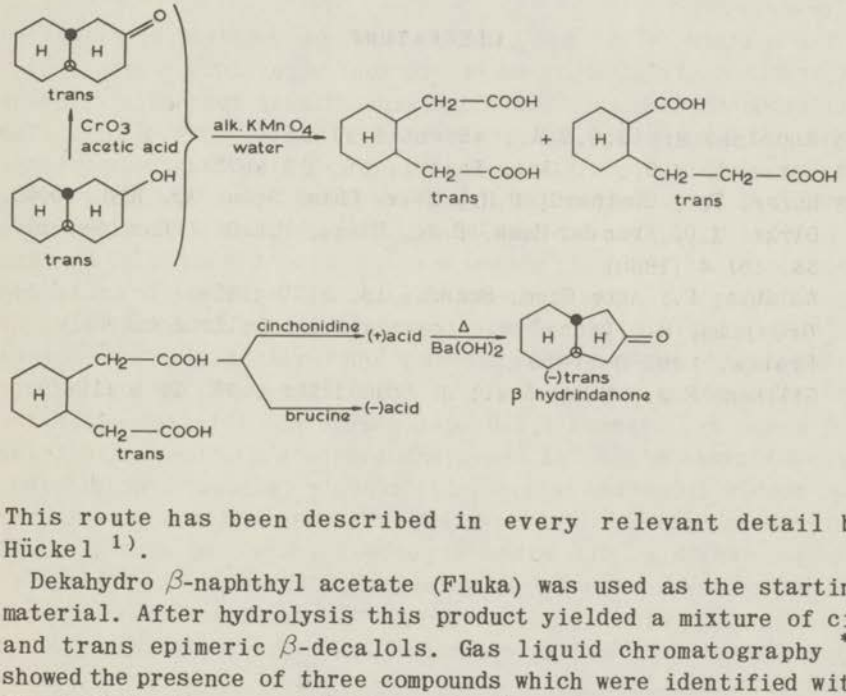
Gillham, E.J., King, R.J.; J. Sci. Instr., 38, 21-5 (1961)

APPENDIX

SYNTHESIS OF OPTICALLY ACTIVE TRANS β-HYDRINDANONE.

Trans β-hydrindanone was prepared from trans β-decalone and trans β-decalol according to the following scheme:



This route has been described in every relevant detail by Hückel [1)].

Dekahydro β-naphthyl acetate (Fluka) was used as the starting material. After hydrolysis this product yielded a mixture of cis and trans epimeric β-decalols. Gas liquid chromatography *) showed the presence of three compounds which were identified with three of the four possible isomeric β-decalols:

trans β-decalol, mp. 53° (probably 2a-ol)
trans β-decalol, mp. 75° (probably 2e-ol)
cis β-decalol, mp. 105° (probably 2e-ol)

The isolation of cis mp. 105° and trans mp. 75° was achieved by

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*) I am greatly obliged to Mr. L.J. Dukker for the very valuable assistance he rendered in carrying out the required gas liquid chromatographical analyses.

a combination of distillation and crystallization procedures. Distillation through a ringpacked column of 1 m length (Todd-column) gave fractions boiling in the range 112-125°/18 mm.

Fractions 112-116°/18 mm contained trans mp. 53° as the principal component. A crystalline alcohol was not isolated however, but the mixture of isomers was oxidized directly to β-decalone.

Fractions 116-120°/18 mm yielded crystalline trans mp. 75° which was purified by repeated crystallization from light petroleum. Fraction 120-125°/18 mm yielded crystalline cis mp. 105°; this alcohol also crystallized from the distillation residue.

The mixture of cis and trans β-decalone obtained by oxidation of fractions 112-116°/18 mm was further separated. Repeated distillation through the Todd column and finally through a spinning band column yielded trans β-decalone, n_D^{20} 1,4824-1,4826. The purity of this product was checked by gas liquid chromatography; samples of lower refractive index were found to contain impurities.

Oxidation of trans β-decalol mp. 75° or trans β-decalone gave a mixture of trans cyclohexane 1,2-diacetic acid and trans cyclohexane 1-propionic, 2-carbonic acid. The diacetic acid could be easily purified by repeated crystallization from water.

Resolution of the acid into its optically active components was achieved by treatment with cinchonidine-base; optically pure (+) trans cyclohexane 1,2-diacetic acid was obtained after recrystallization (5x) of the cinchonidine salt. Upon acidifying the mother liquor the less soluble racemic compound precipitated. The remaining acid was extracted with ether after separating of the precipitate. The ether layer was extracted with a small volume of sodium hydroxide solutions. It yielded (-) diacetic acid in an optically impure form. This acid was treated with brucine-base and the diastereomeric acid salt slowly crystallized from this solution.

Pyrolysis [2] of cyclohexane diacetic acids with a catalytic amount $Ba(OH)_2$ yields β-hydrindanones. Trans cyclohexane 1,2-diacetic acid $[\alpha]_D = +47,6$ (lit.: 48.2) gave rise to the (-) ketone with which the described rotation and circular dichroism measurements were performed.

LITERATURE

1) Hückel W., Sachs M.; Ann. **518**, 182 (1935).
2) Barrett J.W., Linstead R.P.; J.Chem.Soc. 1069 (1935).

SUMMARY.

Measurement of optical rotatory dispersion offers unique information regarding molecular geometry and electronic structure, not obtainable with optically inactive compounds.

In the application of the general quantummechanical formula for the rotational strength to specific molecular models the consequent use of the time derivative of the electric moment operator in the calculation of the electric transition moment is of definite advantage. If approximate wave functions are used in the calculation of the electric and magnetic transition moments the errors involved will be similar. Moreover, if the wave functions are expressed as linear combinations, a splitting in partial moments results. Thus, the use of molecular orbitals in L.C.A.O.-approximation leads to the introduction of bond transition moments and corresponding transitional bond orders.

Optical rotatory dispersion is measured of a number of steroids as examples of homonuclear dienes. From the measurements it appeared that the longest wavelength transition in the diene system is responsible for most of the optical activity in the near ultraviolet. The rotational strength of this transition is calculated theoretically for a diene system with twisted carbon-carbon bonds. The result is correct as to the order of magnitude but individual differences appeared difficult to account for.

An extensive study was made of a ketone (β-hydrindanone). Ultraviolet absorption spectra and rotatory dispersion spectra are recorded with solvents of different polarity. Circular dichroism is measured with isooctane as solvent. It is also obtained from the rotatory dispersion by application of the Kramers-Kronig relations. The g-factor is not constant in the band, but the band is described as a superposition of two bands with a constant g-factor each. The longest wavelength band shows pronounced fine structure. This could be identified as a progression in the carbonyl stretching vibration. The experimental estimate of the magnetic transition moment is at least twice as large as that calculated theoretically. Probably the larger part of the electric transition moment is directed along the axis of the carbonyl group. The origin of the electric transition moment is discussed qualitatively.

SAMENVATTING

De bepaling van de dispersie van de optische rotatie is een methode van onderzoek, die gegevens kan verschaffen over de geometrie en de electronenstructuur van optisch actieve verbindingen.

In de interpretatie van de rotatiedispersie heeft het quantummechanische begrip rotatiesterkte een centrale plaats gekregen. Bij het uitwerken van dit begrip op basis van een bepaald model, met name bij de berekening van het electrisch overgangsmoment, heeft een consequente toepassing van de tijdsafgeleide van de operator van het electrisch moment voordelen. Het blijkt onder meer mogelijk bij gebruik van moleculaire golffuncties, die lineaire combinaties van andere golffuncties zijn, het electrisch en magnetisch overgangsmoment te splitsen in partiële momenten. Op grond van een dergelijke splitsing werden in de L.C.A.O.-benadering overgangsbandmomenten en daarmede verband houdende overgangsbandorden ingevoerd.

Van een aantal steroïden met een homonucleair dieen-systeem werd de rotatiedispersie gemeten. Uit de metingen volgt, dat de electronenovergang in de dieengroepering verantwoordelijk is voor een aanmerkelijk deel van de optische activiteit in het nabije ultra-violet. De rotatiesterkte van deze overgang werd berekend voor een model van een dieen, waarbij de banden tussen de koolstofatomen getordeerd zijn. Hierbij werd gebruik gemaakt van de mogelijkheid de overgangsmomenten te splitsen en de berekening te vereenvoudigen door te werken met de genoemde bandmomenten en bandorden. Het resultaat van de berekening gaf naar orde van grootte een redelijke overeenstemming te zien; individuele verschillen daarentegen bleken moeilijk te verklaren.

Een uitgebreide studie werd gemaakt van een keton (β-hydrindanon). Ultra-violet absorptiespectra en rotatiedispersiespectra werden bepaald in oplosmiddelen van uiteenlopende polariteit. Circulair dichroisme werd gemeten in isooctaan als oplosmiddel. Bovendien werd het circulair dichroisme berekend uit de rotatiedispersie door gebruik te maken van de Kramers-Kronig relaties. De g-factor is niet constant over de band; de spectra in absorptie en circulair dichroisme kunnen worden beschreven als een superpositie van twee banden, ieder met een constante g-factor. De langgolvige band vertoont uitgesproken fijnstructuur en kan geïdentificeerd worden met een progressie in de carbonyl-rekvibratie. De waarde van het magnetisch overgangsmoment, berekend uit de spectra, is minstens 2x zo groot als de waarde, die theoretisch berekend werd. Het electrisch overgangsmoment is waarschijnlijk evenwijdig aan de as van de carbonyl-groep. Het mechanisme van het ontstaan van het electrisch overgangsmoment werd kwalitatief besproken.

Op verzoek van de Faculteit van de Wis- en Natuurkunde volgen hier enige gegevens over mijn academische studie.

In 1947 werd, na het doorlopen van het Stedelijk Gymnasium te 's-Gravenhage de studie aan de Rijksuniversiteit te Leiden aangevangen en in october 1951 werd het candidaatsexamen Wis- en Natuurkunde letter F afgelegd.

Het doctoraalexamen scheikunde werd afgelegd in juli 1956. Dit examen omvatte de vakken Theoretische Organische Chemie, Organische Chemie en Physische Chemie, gedoceerd door de Hoogleraren Dr L.J. Oosterhoff, Dr E. Havinga en Dr J.J. Hermans.

Sinds 1953 ben ik verbonden aan de Afdeling voor Theoretische Organische Chemie, aanvankelijk als candidaat-assistent, later doctoraal-assistent en momenteel als assistent buiten bezwaar van 's Rijks schatkist. Hiernaast ben ik sedert 1958 verbonden aan de Nederlandse organisatie voor zuiver-wetenschappelijk onderzoek als medewerker van de Hoogleraar Dr L.J. Oosterhoff. Hierdoor werd ik in staat gesteld onderzoek te verrichten over de optische activiteit van organische verbindingen en een facet van dit gebied voor een proefschrift te bewerken.

De heren H.J.C. Jacobs chem.drs en N.G. Minnaard chem.drs hebben medegewerkt bij het opstellen en toetsen van de meetapparatuur voor rotatiedispersie, alsook bij de uitvoering en het uitwerken van de metingen.

De heren N.A. Rozendaal, C.J. van der Poel en W.C. Bauer hebben onderdelen voor en wijzigingen in de apparatuur ontworpen en uitgevoerd. Ook het overige personeel ben ik veel dank verschuldigd voor hun voortdurende bereidwilligheid, met name de heer W. Moerer, die het tekenwerk voor dit proefschrift verzorgd heeft.

STELLINGEN

1. Ter verklaring van de [illegible] van aromatische [illegible]

   [illegible]

2. De argumentatie, die [illegible] geeft [illegible] bij de [illegible] is aan bedenkingen onderhevig.

   [illegible] Chem.Revs. [illegible]

3. Op basis van de gewoonlijk aan [illegible] toegekende structuren, is geen bevredigende interpretatie mogelijk van de aan deze verbindingen gemeten draaiing en draaiingsdispersie.

   [illegible] J.Chem.Soc., [illegible]
   Dit proefschrift, blz. [illegible]

4. De veronderstelling, dat de structuur van een [illegible]

   [illegible] Bull. Chem.Soc. Japan [illegible]

STELLINGEN

1. Ter verklaring van de fotochemische reductie van aromatische ketonen tot pinacolen verdient het mechanisme, gegeven door Pitts e.a., de voorkeur boven het door Cohen en Boeseken gepostuleerde mechanisme.

   J.N. Pitts, R. Letsinger, R.P. Taylor, G. Rechtenwald en R. Martin; J.Am.Chem.Soc. **81**, 1068 (1959).
   W.D. Cohen, J. Boeseken; Rec.Trav.Chim. **39**, 243 (1920); **40**, 433 (1921).

2. De argumentatie, die Cilento geeft ten gunste van een decetstructuur bij de zwavel in mercaptanen, is aan bedenkingen onderhevig.

   G. Cilento; Chem.Revs. **60**, 147 (1960).

3. Op basis van de gewoonlijk aan pyrocalciferol en isopyrocalciferol toegekende structuren, is geen bevredigende interpretatie mogelijk van de aan deze verbindingen gemeten draaiing en draaiingsdispersie.

   J. Castells, E.R.H. Jones, G.D. Meakins en R. Williams; J.Chem.Soc., 1159 (1959).
   dit proefschrift, Hfd. III.

4. De veronderstelling, dat de structuur van een halfgeleidend ladingsoverdracht-complex van een aromatische verbinding met jodium is opgebouwd uit een regelmatige stapeling van jodiumatomen met op interstitiele plaatsen de aromatische moleculen, is onvoldoende gefundeerd.

   H. Akamatu, Y. Matsunaga en H. Kuroda; Bull. Chem.Soc. Japan **30**, 618 (1957).

5. Het voorkomen van de natuurlijke polynucleotiden in L-helices kan begrepen worden als uitsluitend gevolg van de aanwezigheid van optisch actieve centra in de elementaire bouwstenen.

P. Doty, H. Boedtker, J.R. Fresco, R. Haselkorn en M. Litt; Proc.Nat.Acad.Sci.U.S. **45**, 482 (1959).
W. Hondius Boldingh, Proefschrift Leiden (1960).

6. Het door Bennema e.a. gegeven beeld van het ontstaan van positieve ionen van aromatische verbindingen door bestraling in boorzuurglazen, behoeft een nadere verklaring.

P. Bennema, G.J. Hoijtink, J.H. Lupinski, L.J. Oosterhoff, P. Selier en J.D.W. van Voorst; Mol.Phys. **2**, 431 (1959).

7. Indien men uit spectroscopische metingen aan moleculen in oplossing moleculaire grootheden wil afleiden, kan bij polaire oplosmiddelen een model voor het werkende veld, dat structuur in de oplossing verdisconteert, van belang zijn.

8. Het verdient aanbeveling ook chromatografie als analysemethode in de Pharmacopee op te nemen.

9. De wet van Parkinson is ook geldig voor de organisatie van inrichtingen voor wetenschappelijk onderwijs en onderzoek.

C. Northcote Parkinson, Parkinson's Law or the Pursuit of Progress. John Murray, London (1958).