OPTICAL ROTATORY POWER

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In 1812 Biot discovered[1] that quartz crystals rotate the plane of linearly polarized light, and subsequently substances such as the terpenes and the sugars, whether in the solid, liquid, or vapour phase, were found[2] to possess the same property. Biot introduced[3] the modern definition of specific rotatory power, $[\alpha]$, which he believed to be a constant property of an optically active molecule, namely,

$$[\alpha] = \alpha/ldp, \tag{1}$$

where α is the observed rotation in degrees, l the path length in decimetres, d the density of the medium, and p the fraction by weight of the optically active substance.

The optical rotation was attributed by Fresnel[4] to the different refractive indices of the active medium for left- and for right-circularly polarized light,

$$\alpha = (n_l - n_r)\pi/\lambda, \tag{2}$$

where λ is the wavelength of the incident light, n_l and n_r are the refractive indices for left- and right-circularly polarized light, respectively, and α is the rotation in radians per unit length, measured in the same units as λ. Plane-polarized light may be resolved into two circular components with equal amplitudes. For circularly polarized light of frequency ν, propagated in the z-direction through a medium of refractive index n, the amplitudes, a, of the radiation field are

$$a = a_0[\mathbf{x} \cos 2\pi(t - nz/c) \mp \mathbf{y} \sin 2\pi(\mathrm{t} - nz/c)], \tag{3}$$

where t is the time and c is the velocity of light in a vacuum. The upper sign on the right-hand side of epuation (3) refers to right- and the lower to left-circularly polarized light, and $\mathbf{x}$ and $\mathbf{y}$ are unit vectors perpendicular to $\mathbf{z}$, forming a right-handed system.

At a given time, say $t = 0$, the envelope of the amplitudes has the form of a right-handed helix about the z-direction for right- and a left-handed helix for left-circularly polarized light (Fig. 1). At a given point, say $z = 0$,

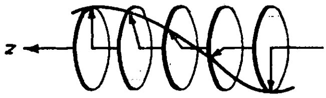

Fig. 1. *Right-circularly polarized light.*

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[1] Biot, *Mem. Inst.*, 1812, **1**, 1.
[2] Biot, *Mem. Acad. Sci.*, 1835, **13**, 39.
[3] Biot, *Mem. Acad. Sci.*, 1838, **15**, 93.
[4] Fresnel, *Ann. Chim. Phys.*, 1825, **28**, 147.

the vector amplitudes appear, to an observer looking in the $-z$ direction, to be rotating clockwise for right- and anticlockwise for left-circularly polarized light (Fig. 2). If the refractive index, n, is larger for left- than for right-circularly polarized light, the former component is relatively delayed in traversing the medium, giving rise to a dextrorotation of the plane-polarized resultant of the two circular components (Fig. 2).

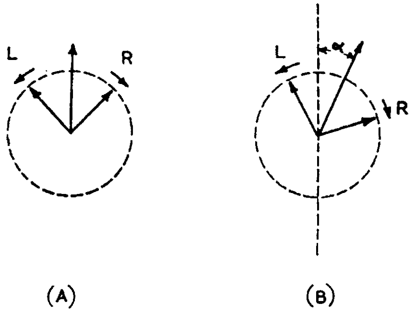

FIG. 2. *Left- and right-circularly polarized light, and the plane-polarized resultant, (A) before, and (B) after, traversing an optically active medium.*

Further, if the refractive index, n, is larger for left- than for right-circularly polarized light at wavelengths where the optically active medium is transparent, the absorption index, k, should be larger for left- than for right-circularly polarized light at absorption frequencies. The latter phenomenon, circular dichroism, was observed by Haidinger[5] in crystals of amethyst quartz, and by Cotton[6] in solutions of copper(II) and chromium(III) (+)-tartrate. The "Cotton effect," as the phenomenon came to be termed,[7-11] is manifest, not only by the differential absorption of left- and right-circularly polarized light, but also by the anomalous dispersion of the optical rotation, and by the ellipticity of the light used to measure the rotation, in the absorption wavelength region (Fig. 3).

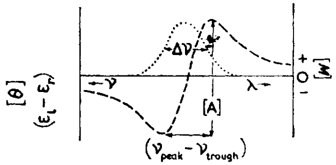

FIG. 3. *The circular dichroism (........) and the anomalous rotatory dispersion (----) given by a dissymmetric compound in the absorption wavelength region.*

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[5] Haidinger, *Ann. Phys.*, 1847, **70**, 531.

[6] Cotton, *Compt. rend.*, 1895, **120**, 989, 1044.

[7] Mitchell, "The Cotton Effect," Bell, London, 1933.

[8] Lowry, "Optical Rotatory Power," Longmans, Green and Co., London, 1935.

[9] Kuhn, "Stereochemie," ed. Freudenberg, Deuticke, Leipzig, 1933.

[10] Jaeger, "Spatial Arrangements of Atomic Systems and Optical Activity," McGraw-Hill, New York, 1930.

[11] Mathieu, "Les Theories Moleculaires du Pouvoir Rotatoire Naturel," Gauthier-Villars, Paris, 1946; "Handbuch der Physik," ed. Flugge, Springer, Berlin, 1957.

Owing to the differential absorption at resonant frequencies, the two circular components, after traversing the optically active medium, combine to give elliptically polarized light (Fig. 4). The optical rotation, α, is given by the angle between the plane of the incident linearly polarized light and the major axis of the emergent elliptically polarized light, whilst the ratio of the minor to the major axis of the ellipse measures the tangent

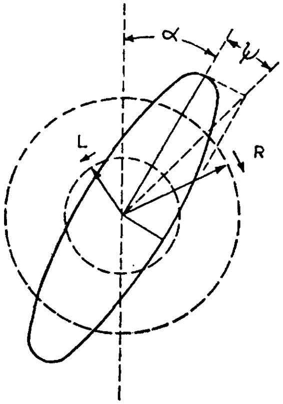

FIG. 4. *The rotation, α, and the ellipticity, ψ, of plane-polarized light emerging from an optically active medium in the absorption wavelength range.*

of the angle of ellipticity, ψ (Fig. 4). The major and the minor axis of the ellipse are, respectively, the sum and the difference of the amplitudes of the two circular components on emerging from the optically active medium, so that

$$\tan \psi = (a_r - a_l)/(a_r + a_l). \tag{4}$$

For unit path length, the amplitudes, a, are related to the absorption indices, k, by

$$a = a_0 \exp(- 2\pi k/\lambda). \tag{5}$$

In general, the angle of ellipticity, ψ, and the circular dichroism, $k_l - k_r$, are small, and equations (4) and (5) give in good approximation,

$$\psi = (k_l - k_r)\pi/\lambda, \tag{6}$$

with ψ measured in radians per unit path length.

Experimentally, decadic molar extinction coefficients, $\epsilon = (1/cl) \log_{10} (I_0/I)$, are more commonly used than absorption indices, and ellipticities are measured in degrees rather than in radians. The specific ellipticity, $[\psi]$, is defined, by analogy with the specific rotation, as

$$[\psi] = \psi/ldp, \tag{7}$$

where ψ is measured in degrees and the remaining quantities have the same significance as in equation (1). Similarly the molecular ellipticity, $[\theta]$, is defined as

$$[\theta] = [\psi]M/100, \tag{8}$$

by analogy with the molecular rotation, $[M]$,

$$[M] = [\alpha]M/100, \tag{9}$$

where M is the molecular weight of the optically active compound. The conversion factors then give the relation between the molecular ellipticity in degrees and the decadic molar circular dichroism as

$$[\theta] = 3300(\epsilon_l - \epsilon_r). \tag{10}$$

Biot found [12] that at long wavelengths, outside the absorption region, the angle of rotation given by an optically active substance was inversely proportional to the square of the wavelength. The relation is not exact, and Drude showed[13] that the rotation at long wavelengths may be more precisely represented by a sum of the contributions from a number of circular dichroism bands, each with an absorption maximum, λ_i,

$$[\alpha]_\gamma = \Sigma C_i/(\lambda^2 - \lambda_i^2), \tag{11}$$

where C_i is a constant characteristic of the circular dichroism band at λ_i.

Drude's equation (11) for normal rotatory dispersion does not hold at wavelengths in the absorption region, since the rotation does not go to $\mp\infty$ at λ_i (Fig. 3). The anomalous rotatory dispersion observed in the wavelength region of an absorption band at λ_0 is given by the dominant contribution of a single term from Drude's equation, modified to allow for the finite band width of the absorption by the damping factor, G:

$$[\alpha]\lambda = D(\lambda^2 - \lambda_0^2)/[(\lambda^2 - \lambda_0^2)^2 + G\lambda^2], \tag{12}$$

together with subsidiary contributions from absorption bands at different wavelengths, providing a normal background rotatory dispersion superimposed upon the anomaly.

The anomalous rotatory dispersion curve represents essentially the derivative of the circular dichroism curve with respect to frequency (Fig. 3). The dispersion–absorption relations of Kuhn[9,14] show that the amplitude $[A]$ of the anomaly in the rotatory dispersion curve is related to the maximum circular dichroism by

$$[A] = [M]_{\text{max.}} - [M]_{\text{min.}} = 4028(\epsilon_l - \epsilon_r)_{\text{max.}}, \tag{13}$$

and that the difference between the frequencies of the peak and the trough

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[12] Biot, *Mem. Acad. Sci.*, 1817, **2**, 41.

[13] Drude, "Lehrbuch der Optik," Leipzig, 1900, English translation, Dover, New York, 1959.

[14] Kuhn, *Ann. Rev. Phys. Chem.*, 1958, **9**, 417.

in the dispersion curve is related to the band width, $\Delta\nu$, at half maximum circular dichroism (Fig. 3), by

$$\Delta\nu = 0{\cdot}925\,(\nu_{\text{peak}} - \nu_{\text{trough}}). \qquad (14)$$

These relations are based on the assumption that the circular dichroism curve is Gaussian in form.

Theories of Optical Rotatory Power.—Herschel[15] observed that crystals of quartz with rotatory powers of opposite sign had hemihedral faces which were related, in the two types of crystal, as mirror images. The crystals of optical isomers were found to have similarly related hemihedral faces, and on this basis Biot's pupil, Pasteur,[16] divided molecules into two classes: those with superposable mirror images, and those with mirror images that were non-superposable, the latter forming the class of dissymmetric molecules with optical rotatory power. Pasteur[17] speculated that the dissymmetry might arise from a helical molecular structure, or from an irregular tetrahedral arrangement of the constituent atoms. The former suggestion was taken up as a physical model by Drude,[13] and the latter as a chemical model by Le Bel[18] and van't Hoff.[19]

The tetrahedral model for the carbon atom was dependent upon the available optical-rotation evidence, and, in turn, the model enabled van't Hoff to distinguish two main types of optically active organic compound: those containing an asymmetric carbon atom, and those of the spiran and allene type which are structurally dissymmetric but contain no single asymmetric centre.[19] Similarly, optical-rotation data established the octahedral model for hexaco-ordinated transition-metal complexes, the model allowing Werner[20] to distinguish two main types of molecular dissymmetry, namely, the dihedral complexes, and the *cis*-complexes with two chelate bridges and two monofunctional ligands.

Adopting the helical model, Drude showed[13] that, if a charged particle is displaced along a helical path, the translatory motion gives rise to an electric dipole moment and the rotatory motion to a magnetic dipole moment. The two moments are parallel or antiparallel according to the right or left chirality (handedness) of the helical path. In left- and right-circularly polarized light the electric field and the time-derivative of the magnetic field are parallel and antiparallel, respectively, so that, for a molecule containing an electron constrained to move in a right-handed helical path, the refractive index in the transparent long-wavelength region and the extinction coefficient at absorption frequencies should be larger for left- than for right-circularly polarized light if the radiation is incident

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[15] Herschel, *Trans. Cambridge Phil. Soc.*, 1822, **1**, 43.
[16] Pasteur, *Ann. Chim. Phys.*, 1848, **24**, 443.
[17] Pasteur, Alembic Club Reprint, No. 14, Edinburgh, 1910.
[18] Le Bel, *Bull. Soc. chim. France*, 1874, **22**, 337.
[19] van't Hoff, "Chemistry in Space," Clarendon Press, Oxford, 1891.
[20] Werner, *Ber.*, 1911, **44**, 1887.

perpendicular to the axis of the helix.[21] That is, the molecule should possess a positive rotatory power. Conversely, the molecule should have a negative rotatory power if the helical path of the electron is left-handed.

The particular details of Drude's theory were criticised by Born[22] and Kuhn[23] on the grounds that the mathematical formalism did not correspond exactly to the physical model, but all physical theories of optical rotatory power have the fundamental requirement that the electronic motions induced by the radiation should possess an electric and a magnetic moment with parallel or antiparallel components. As a result of these criticisms it was generally held[8, 9] that optical rotatory power could not be explained by a one-particle model, and a number of multiparticle models were put forward, notably, the coupled-oscillator[22-26] and the polarizability[27, 28] theory, in which the electric and the magnetic moment associated with optical activity arose from non-parallel electronic vibrations in the different groups of a given molecule.

The quantum-mechanical theory, developed in general terms by Rosenfeld,[29] ascribes the optical rotatory power of a molecule to electronic transitions which have parallel or antiparallel electric and magnetic transition moments. The theory defines[30] a quantity governing the rotatory power of a transition between the electronic states a and b of a molecule, the rotational strength, R_{ba}, as the scalar product of the electric and the magnetic dipole transition moments,

$$R_{ba} = Im(a|\mathbf{P}|b)(b|\mathbf{M}|a), \tag{15}$$

where a and b are the wave functions of the two electronic states, and $\mathbf{P}$ and $\mathbf{M}$ are, respectively, the electric and the magnetic dipole operators, and Im signifies that the imaginary part of the product is to be taken.

The magnetic moment operator contains the imaginary quantity, i,

$$\mathbf{M} = (-\boldsymbol{ieh}/4\pi \boldsymbol{mc})\cdot \mathrm{d}/\mathrm{d}\phi, \tag{16}$$

where $\boldsymbol{e}$ and $\boldsymbol{m}$ are, respectively, the charge and the mass of the electron, $\boldsymbol{h}$ is Planck's constant, $\boldsymbol{c}$ the velocity of light, and ϕ the angle of rotation about a given axis. However, the electric moment operator is real, namely,

$$\mathbf{P} = \boldsymbol{e}\mathbf{r} \tag{17}$$

where $\mathbf{r}$ is a vector defining the position of the electron, and, when real wave functions are used, equation (15) gives a rotational strength which is

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[21] Kauzmann, Walter, and Eyring, *Chem. Rev.*, 1940, **26**, 339.
[22] Born, *Phys. Z.*, 1915, **16**, 251.
[23] Kuhn, *Z. phys. Chem.*, 1933, *B*, **20**, 325.
[24] Kuhn, *Z. phys. Chem.*, 1929, *B*, **4**, 14.
[25] Oseen, *Ann. Phys.*, 1915, **48**, 1.
[26] Lande, *Ann. Phys.*, 1918, **56**, 225.
[27] De Mallemann, *Rev. sci.*, 1927, **38**, 453.
[28] Boys, *Proc. Roy. Soc.*, 1934, *A*, **144**, 655.
[29] Rosenfeld, *Z. Phys.*, 1928, **52**, 161.
[30] Condon, *Rev. Mod. Phys.*, 1937, **9**, 432.

real, as required for any observable physical property of a molecule.

For practical purposes, equation (15) may be written,

$$R_{ba} = \rho\mu \cos \theta, \tag{18}$$

where ρ and μ are, respectively, the real electric and magnetic transition moments, and θ is the angle between the directions of the two moments.

Experimentally the rotational strength of an electronic transition may be obtained[31] from the area of the corresponding circular dichroism band:

$$\begin{aligned} R_{ba} &= (3\boldsymbol{hc}\ 10^3 \log_e 10/32\pi^3 N) \int[(\epsilon_l - \epsilon_r)/\nu]\mathrm{d}\nu \\ &= 22{\cdot}9 \times 10^{-40} \int[(\epsilon_l - \epsilon_r)/\nu]\mathrm{d}\nu, \end{aligned} \tag{19}$$

where ν is the absorption frequency, the rotational strength being given in c.g.s. units. Equally the rotational strength may be obtained from the measured ellipticity or the anomalous rotatory dispersion through equations (10), (13), and (14).

The rotational strength is a quantity analogous to the dipole strength, D_{ba}, which, for a given transition, represents the sum of the squares of the electric dipole, the magnetic dipole, and the multipole transition moments. The dipole strength is given, in c.g.s. units, from the area of the corresponding absorption band by

$$\begin{aligned} D_{ba} &= (3\boldsymbol{hc}\ 10^3 \log_e 10/8\pi^3 N) \int(\epsilon/\nu)\mathrm{d}\nu \\ &= 91{\cdot}8 \times 10^{-40} \int(\epsilon/\nu)\mathrm{d}\nu \end{aligned} \tag{20}$$

The classical oscillator strength, f, giving the number of electrons promoted in the transition responsible for the absorption band, is related to the dipole strength by the expression

$$\begin{aligned} f_{ba} &= 8\pi^2 \boldsymbol{mc}\nu D_{ba}/3\boldsymbol{he}^2 \\ &= 0{\cdot}476 \times 10^{30} \nu D_{ba}. \end{aligned} \tag{21}$$

The rotational and oscillator strengths of the electronic transitions of a given molecule are subject to sum rules, which were derived classically and quantum-mechanically. Kuhn[24] and then Condon[30] showed that the sum of the rotational strengths of all the electronic transitions occurring in any given molecule vanishes identically,

$$\underset{\text{all transitions}}{\Sigma R_{ba}} = 0. \tag{22}$$

Since the molecular rotation of a molecule at a particular frequency is the sum of contributions from all of the electronic transitions,

$$[M]_\nu = [96\pi N(n^2 + 2)/3\boldsymbol{hc}]\ \underset{i}{\Sigma} R_i \nu_i^2/(\nu_i^2 - \nu^2), \tag{23}$$

the optical rotation vanishes at zero and at infinite frequency.

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[31] Moffitt and Moscowitz, *J. Chem. Phys.*, 1959, **30**, 648.

In contrast, the sum of the oscillator strengths of all the electronic transitions given by a particular molecule should equal the number of valency electrons,

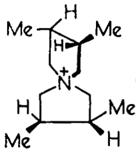
$$\sum_{\text{all transitions}} f_{ba} = n, \tag{24}$$

as was shown by Kuhn[32] and Thomas.[33] The sum of the oscillator strengths may be obtained from the variation of refractive index with frequency,

$$(n_v^2 - 1)/(n_v^2 + 2) = (Ne^2d/3\pi mM)\sum_{i} f_i/(\nu_i^2 - \nu^2) \tag{25}$$

and it is found[34] that the sum, $\sum_i f_i$, has a value in the region of one-half to one-third of the number of electrons in the valency shells.

Spectroscopic Selection Rules and Optical Activity.—Pasteur's criterion[16] for optical rotatory power, that the molecule should exist in two isomeric forms related as non-superposable mirror-images, was subsequently elaborated[35] into three stereochemical symmetry conditions for optical activity. These are that the molecule should be devoid of a centre of inversion, a plane of symmetry, and an alternating rotation-reflection axis of symmetry. The importance of the last requirement is illustrated[36] by the optically inactive spiran (1), which has neither a centre of inversion nor a plane of symmetry but is superposable upon its mirror image as it has a four-fold alternating axis of symmetry (it belongs to the point group, S_4). In a formal sense the absence of a rotation-reflection axis of symmetry is the fundamental stereochemical requirement for optical activity, since a one-fold alternating axis is equivalent to a plane of symmetry and a two-fold alternating axis is identical with a centre of inversion.



(1)

The stereochemical requirements for optical activity are coincident with the symmetry conditions which allow an electronic transition to have electric and magnetic moments with a common direction. An electric dipole transition involves the linear displacement of charge. In the case of the atomic transition, $s \rightarrow p_z$ (Fig. 5), electronic charge undergoes a translatory motion in the z-direction, and inversion through the centre, or reflection in the xy-plane or in any plane perpendicular to the z-direction, reverses the direction of that motion. The displacement is governed by the

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[32] Kuhn, *Z. Phys.*, 1925, **33**, 408.
[33] Thomas, *Naturwiss.*, 1925, **13**, 627.
[34] Lowry, *Proc. Roy. Soc.*, 1931, *A*, **133**, 188.
[35] Voigt, *Ann. Phys.*, 1905, **18**, 649.
[36] McCasland and Proskow, *J. Amer. Chem. Soc.*, 1956, **78**, 5646.

electric moment operator, **P** (eqn. 17), which is antisymmetric with respect to inversion and to reflection in planes perpendicular to the direction of operation, possessing the symmetry properties of a translatory motion in that direction, *e.g.*, T_z in the case of a $s \rightarrow p_z$ transition (Fig. 5). The electric dipole transition moment, $(a|\mathbf{P}|b)$ (eqn. 15), must be invariant with respect to any inversion, reflection, or rotation of the electron's co-ordinate system, as it is a physical property of the molecule, and this condition requires that the direct product of the symmetries of the wave functions, *a* and *b*, belongs to a symmetry representation containing a translatory motion (Table 1), *e.g.*, the representation containing T_z for the $s \rightarrow p_z$ transition.

TABLE 1. *Selection rules for electronic transitions.*

	Electric dipole	Magnetic dipole
Hydrogenic atoms:		
main quantum number	Δn = any value	$\Delta n = 0$
subsidiary quantum number	$\Delta l = \pm 1$	$\Delta l = 0$
magnetic quantum number	$\Delta m = 0, \pm 1$	$\Delta m = 0, \pm 1$
electron spin	$\Delta s = 0$	$\Delta s = 0$
Symmetries of the electronic states connected:		
inversion	$u \longleftrightarrow g$	$g \longleftrightarrow g$ $u \longleftrightarrow u$
reflection, or rotation-reflection	$+ \longleftrightarrow -$	$+ \longleftrightarrow +$ $- \longleftrightarrow -$
Direct product of the state symmetries transforms as:	A translation	A rotation

A magnetic dipole transition entails the rotatory displacement of charge, as in the case of the atomic transition, $p_x \rightarrow p_y$ (Fig. 5), where the electronic charge undergoes a rotation about the *z*-axis. An inversion through the centre or a reflection through any plane perpendicular to the rotation axis does not change the sense of the rotation. The magnetic moment operator, **M** (eqn. 16), is symmetric with respect to inversion and to reflection through planes perpendicular to the operative axis, transforming as a rotation about that axis, *e.g.*, R_z in the case of the $p_x \rightarrow p_y$ transition (Fig. 5). The magnetic dipole transition moment, $(b|\mathbf{M}|a)$ (eqn. 15). being a physical property, is unchanged by any rotation, inversion, or reflection of the axes to which the electronic co-ordinates refer, so that the direct product of the symmetries of the electronic wave functions, *a* and *b*, must belong, in this case, to a representation containing a rotation (Table 1), *e.g.*, the representation containing R_z for the $p_x \rightarrow p_y$ transition.

The electronic wave functions, *a* and *b*, of a given atom or molecule cannot have symmetries giving a direct product which is simultaneously symmetric and antisymmetric with respect to an inversion, reflection, or rotation-reflection operation, and an electronic transition having an electric and a magnetic moment which are parallel or antiparallel is not possible in a molecule containing a centre, a plane, or an alternating axis. In an optically active molecule, devoid of these symmetry elements, perturbations arising from the atoms conferring dissymmetry upon the molecule mix the electric and the magnetic dipole excitations, and the resultant composite electronic transitions, in general, have a finite rotational strength. Thus the mixing of the $s \rightarrow p_z$ and the $p_x \rightarrow p_y$ excitations at a given atomic centre in a dissymmetric molecule would give a composite transition with a non-zero rotational strength in the z-direction, the rotational strength being positive for the parallel orientation of the component magnetic and electric transition moments in one optical isomer, and negative for the antiparallel orientation of the component moments in the enantiomer.

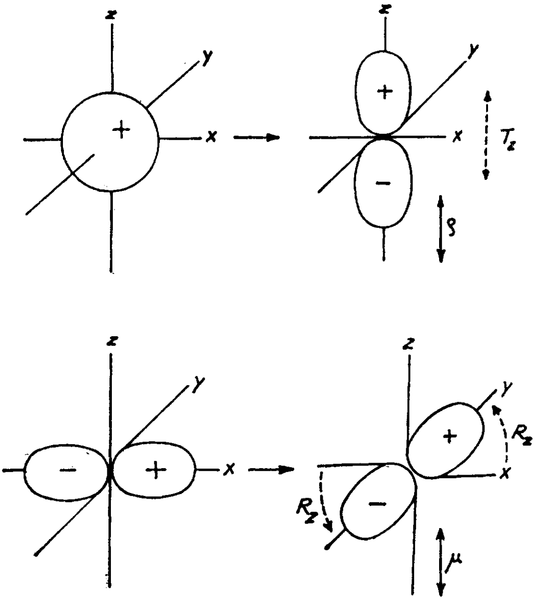
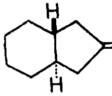


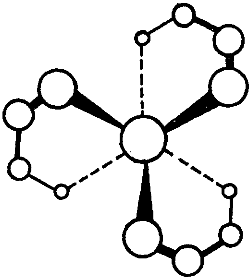
FIG. 5. *The electronic transitions, $s \rightarrow p_z$ and $p_x \rightarrow p_y$, and the directions of the respective electric, ρ, and magnetic, μ, transition moments. T_z = translation in the z-direction, and R_z = rotation about the z-axis.*

Many optically active molecules are devoid of any element of symmetry, but optical rotatory power is consistent with all of the purely rotational symmetry elements. In the dihedral symmetry groups, D_p, which have a principal p-fold rotation axis, C_q, and p two-fold rotation axes, C_2, perpendicular to the C_p axis at equal angles to one another, translations along, and rotations about, a given axis transform under a common symmetry representation, and in any molecule belonging to a dihedral point group most of the electronic transitions with a finite dipole strength have a non-zero rotational strength. Thus in the ketone (2),


(2)

which belongs to the point group D_1 ($\equiv C_2$), containing a single two-fold rotation axis in the z-direction along the carbonyl bond, both of the oxygen-atom transitions, $2s \rightarrow 2p_z$ and $2p_x \rightarrow 2p_y$, belong to the symmetry representation A, which contains both T_z and R_z.

The dihedral optically active molecules, such as the ketone (2), or the transition-metal complexes with three bidentate ligands, *e.g.* (3), which


(3)

belong to the group D_3, containing one C_3 and two C_2, are of particular importance. The moments of a given electronic transition in a dihedral molecule are directed either parallel or perpendicular to the principal rotation axis, and the angle, θ (eqn. 18), between the directions of the electric and the magnetic moment is readily evaluated, as will be shown below, whereas in optically active molecules lacking a two-fold or higher rotation axis the orientation of the transition moments is not symmetry-determined, and the evaluation of the angle, θ (eqn. 18), is more devious.

Stereochemical and Spectroscopic Applications.—Classical stereochemistry was grounded upon the study of optical rotatory power. However, it was the existence of the phenomenon that established the tetrahedral structure of the saturated carbon atom and the octahedral structure of the hexaco-ordinated metal complex, and, until recently, studies of the sign and the magnitude of the optical rotation given by dissymmetric molecules yielded relatively few unambiguous stereochemical applications.Before the establishment of the absolute configuration of (+)-tartaric acid[37] and the (+)-cobalt(III) trisethylenediamine complex[38] by X-ray diffraction methods, a number of attempts were made

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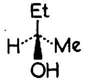
[37] Bijvoet, Peerdeman, and van Bommel, *Nature*, 1951, **168**, 271.

[38] Nakatsu, Shiro, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158.

to relate the sign of the rotatory power to the chirality of dissymmetric organic compounds and metal complexes, but different models did not always assign the same configuration to a given enantiomer. For example, different theories variously ascribed a dextrorotatory[28,39] and a lævorotatory power[40,41] to L(−)-butan-2-ol (4).



(4)

Optical rotation is essentially a spectroscopic phenomenon, and an incomplete knowledge of the electronic transitions giving rise to the absorption of radiation and to the rotatory power limited the early attempts to determine optically the absolute configuration of dissymmetric molecules.The first major generalisation relating rotatory power to chirality, the octant rule for dissymmetric ketones,[42] was based in part upon results derived from spectroscopic studies of the 3000 Å carbonyl absorption, and the chirality rule for dihedral d^3 and d^6 transition metal complexes[43] is a wholly spectroscopic criterion.

Measurements of circular dichroism and optical rotatory dispersion provide information which characterises in more detail than do simple absorption measurements the electronic transitions responsible for the absorption and the rotatory power, and in turn the characterisation of the transitions may assist stereochemical studies. An important spectroscopic application of circular-dichroism measurements is the identification of magnetic-dipole transitions. In principle, the electronic transitions of polyatomic molecules related to atomic transitions of the $p \rightarrow p$, $d \rightarrow d$, and $f \rightarrow f$ types are allowed in magnetic dipole radiation fields, but frequently an extraneous electric transition moment prevents the characterisation of the transition by methods depending upon the detection of a magnetic dipole strength.

For compounds of the rare-earth ions magnetic dipole transitions of the $f \rightarrow f$ type have been identified in two ways: first, from the plane-polarized absorption spectrum of the crystal;[44] and, secondly, from the wide-angle interference pattern given by the emission from a thin film of the compound in solution.[45] The *f*-electrons of a rare-earth ion are well shielded from the molecular environment, but not completely. The interference fringes given by the magnetic dipole emission of the europic ion at 5880Å become considerably blurred, for example, when the emission source is

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[39] Kirkwood, *J. Chem. Phys.*, 1937, **5**, 479.
[40] Kuhn, *Z. phys. Chem.*, 1935, *B*, **31**, 18.
[41] Condon, Altar, and Eyring, *J. Chem. Phys.*, 1937, **5**, 753.
[42] Moffitt, Woodward, Moscowitz, Klyne, and Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.
[43] Ballard, McCaffery, and Mason, *Proc. Chem. Soc.*, 1962, 331.
[44] Sayre, Sancier, and Freed, *J. Chem. Phys.*, 1955, **23**, 2060.
[45] Freed and Weissman, *Phys. Rev.*, 1941, **60**, 440.

changed from europium(III) nitrate in glycerol to the europium(III)-tris-salicylaldehyde complex in benzene solution,[45] owing to an extraneous electric moment arising from the reduction in symmetry of the molecular environment.

In the $d \rightarrow d$ transitions of metal complexes and the $n_p \rightarrow \pi$ transitions of organic molecules the extraneous electric moment dominates the absorption, and the methods used to identify magnetic dipole transitions in compounds of the rare-earth ions are impracticable for these cases. Transition moments allowed by the selection rules have values of the order of the Bohr magneton ($9{\cdot}3 \times 10^{-21}$ c.g.s.) and of the product of the electronic charge and a bond distance ($\sim 10^{-17}$ c.g.s.) for the magnetic dipole and the electric dipole case, respectively. Accordingly, a pure magnetic dipole transition should have an oscillator strength of the order of 10^{-6}, compared with an order of unity for an electric dipole transition.

However, the $d \rightarrow d$ and $n \rightarrow \pi$ transitions which are magnetic dipole allowed in principle are found to have oscillator strengths of the order of 10^{-4} or greater, like the transitions of metal complexes or of organic molecules, such as the $\Sigma_g^+ \rightarrow \Sigma_u^-$, Δ_u excitations of polyacetylenes,[46] which are forbidden by the selection rules for both electric and magnetic dipole radiation fields. In all these cases most of the absorption intensity is borrowed from an electric dipole transition of higher energy, owing to perturbations arising from the low symmetry of the molecular environment of the chromophore. The low symmetry may be static, deriving from the particular stereochemistry of the molecule, or dynamic, occurring only at the turning points of the non-totally symmetric vibrations in molecules of high symmetry.

Although the magnetic contribution to the total dipole strength of a $d \rightarrow d$ or $n \rightarrow \pi$ transition may be too small to be measured, the rotational strength of such a transition in a dissymmetric molecule may be readily determined. The magnetic moment may be evaluated from the experimental rotational and dipole strengths (eqns. 19 and 20) if the angle, θ (eqn. 18), is eliminated by the study of a dihedral molecule. The value obtained may be used to estimate the angle, θ, for the corresponding transition of the same chromophore in a dissymmetric molecule lacking an element of symmetry. If the latter molecule owes its dissymmetry to a single or a dominant substituent, the estimated angle, θ, gives the disposition of that substituent relative to the chromophore.

An approximate experimental criterion for a magnetic dipole transition is provided by the ratio, g, of the circular dichroism to the absorption, termed the dissymmetry factor by Kuhn,[47]

$$g = (\epsilon_l - \epsilon_r)/\epsilon \tag{26}$$

$$\approx 4R_{ba}/D_{ba} = 4\rho\mu \cos\theta/\rho^2. \tag{27}$$

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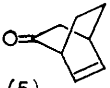
[46] Mason, *Quart. Rev.*, 1961, **15**, 287.
[47] Kuhn, *Trans. Faraday Soc.*, 1930, **46**, 293.

Transitions which are forbidden in both electric and magnetic dipole radiation fields may be expected to acquire extraneous electric and magnetic moments with approximately the same fractional value of the Debye and of the Bohr magneton, respectively, and the g-factor should not exceed a value of about 0·01 in such cases.[48] For magnetic dipole transitions the g-factor should have a larger value if θ, or its supplement, is a small angle. Observed values of the g-factor range up to[49] 0·4, the maximum possible value being 2.

Electronic transitions may be characterised further by the relations between the rotational strength and the dipole strength of a given transition in a related series of compounds. For a particular magnetic dipole transition, the magnetic moment is approximately constant in the series of compounds, but the extraneous electric moment, given by the square root of the dipole strength, may vary quite widely. In this case the relation is,

$$R_{ba} = \mu \cos \theta . \sqrt{D_{ba}} \tag{28}$$

The rotatory powers and the absorption intensities of the bicyclic unsaturated ketones[50] (5) and (6), and of parasantonide[50,51] (7), in the 3000 Å region follow eqn. (28), the logarithmic plot of the amplitude of the rotatory dispersion against the extinction coefficient having a slope of 0·5 (Fig. 6). Since the carbonyl $n \rightarrow \pi$ transition has a magnetic moment directed along the carbonyl bond axis, of [52] 1·0β_M, where β_M is the Bohr magneton, the angle, θ, has a value of ~40° for the 3000 Å absorption of the ketones (5), (6), and /7), supporting the view,[53] suggested on theoretical grounds, that the extraneous electric moment originates from the carbon–carbon double bond.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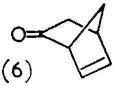
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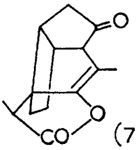

(7)

For an electric dipole transition in a related series of dissymmetric compounds, as in the case of a $\pi \rightarrow \pi$ transition of a twisted diene or a hindered biaryl, the rotational strength should increase and the dipole strength should fall as the angle of twist is increased from zero to $\pi/2$. For a transition forbidden in both electric and magnetic dipole radiation fields, the rotational strength should be directly proportional to the dipole

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[48] Mason, *Proc. Chem. Soc.*, 1962, 137.
[49] Rudnick and Ingersoll, *J. Opt. Soc. Amer.*, 1942, **32**, 622.
[50] Mislow and Berger, *J. Amer. Chem. Soc.*, 1962, **84**, 1956.
[51] Mitchell and Schwarzwald, *J.*, 1939, 889.
[52] Mason, *Mol. Phys.*, 1962, **5**, 343.
[53] Labhart and Wagniere, *Helv. Chim. Acta*, 1959, **42**, 2219.

strength, on the assumption that the extraneous electric and magnetic moment are enhanced proportionately by the dissymmetric perturbations in a related series of compounds.

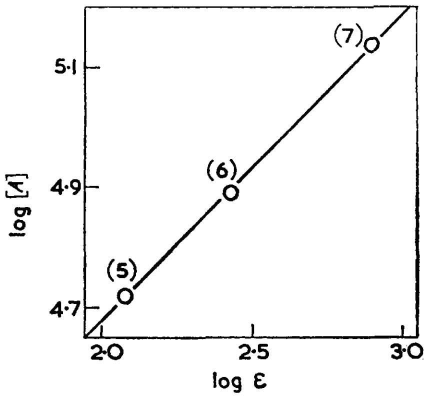

FIG. 6. *The relation between the amplitude of the anomalous rotatory dispersion,* [*A*], *and the extinction coefficient of the* 3000 Å *absorption band,* ε, *of the ketones* (5), (6), *and* (7). *The data are quoted from refs.* 50 *and* 77.

The Rotatory Power of Lone-pair Electron Transitions.—The weak-to-moderate long-wavelength absorption of organic compounds containing heteroatoms is due, in general, to the transition of a lone-pair electron to an antibonding σ- or π-orbital.[46] In principle, such transitions should be magnetic dipole allowed to the degree that they involve a $p \rightarrow p$ atomic transition at the heteroatom. As required by the dissymmetry-factor criterion for magnetic dipole transitions (eqn. 26), the g-factors of $n \rightarrow \pi$ absorption bands attain values of the order of 10^{-2} or greater (Table 2). The available values for $n \rightarrow \sigma$ bands are somewhat lower (Table 2), owing to the smaller $p \rightarrow p$ heteroatom component in a $n \rightarrow \sigma$ transition.

The rotatory powers of the $n \rightarrow \pi$ chromophores are readily accessible experimentally, since the dissymmetry factors are large, and such chromophores were extensively investigated in the classical researches of Lowry,[8] Kuhn,[9] and other workers,[7,11] and in more recent studies.[54] Owing to the prevalence of the carbonyl group in a variety of natural products, the rotatory power of the 3000 Å carbonyl absorption has received particular attention, both experimentally[8,54] and theoretically.[21,42] The one-electron theory of optical rotatory power[30] was early applied to the case of 3-methylcyclopentanone (8) by Kauzmann, Walter, and Eyring.[21] The treatment was based upon the older assignment of the 3000 Å carbonyl absorption to the $n \rightarrow \sigma$ transition, but it was pointed out that an equivalent analysis was possible in terms of the now established[55,56] assignment of the absorption

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[54] Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960.
[55] Brand, *J.*, 1956, 858.
[56] Robinson, *Canad. J. Phys.*, 1956, **34**, 699.

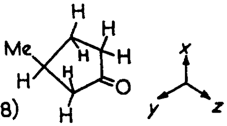
to the $n \rightarrow \pi$ transition, and more recent studies[57] are based on the latter assignment.

TABLE 2. *Electronic absorption spectra and circular dichroism of lone-pair electron transitions.*

Compound	λ_{max} (Å)	ϵ	$(\epsilon_l - \epsilon_r)$	g	Transition		Ref.
3β-Hydroxy-5α-androstan-16-one (13)	3000	34	−5·95	0·175	$>C=O$	$n \rightarrow \pi$	52
3β-Hydroxy-5α-androstan-17-one (15)	2940	40	3·05	0·081	$>C=O$	$n \rightarrow \pi$	*a*
3β-Hydroxy-5α-androstan-17-thione (16)	4820	13	1·27	0·098	$>C=S$	$n \rightarrow \pi$	*a*
(−)-menthyl-dixanthide	3630	66	4·80	0·073	$-S-\overset{\vert}{C}=S$	$n \rightarrow \pi$	*b*
2,2-Dinitrocamphane	2700	300	−3·35	0·012	$>C-NO_2$	$n \rightarrow \pi$	*c*
(−)-menthyl (+)-β-chloro-β-nitroso-butyrate	6350	17·2	0·648	0·038	$>C-NO$	$n \rightarrow \pi$	*d*
(+)-1-Methylheptyl nitrite	3720	60	0·50	0·01	$-O-NO$	$n \rightarrow \pi$	*e*
α-azido-*NN*-dimethyl-propionamide	2800	25	0·45	0·024	$>C-N_3$	$n \rightarrow \pi$	*f*
α-Diazocamphor	4070	19·5	0·255	0·013	$>C=N_2$	$n \rightarrow \pi$	*g*
(+)-1-Methylheptyl iodide	2700	100	0·5	0·005	$>C-I$	$n \rightarrow \sigma$	*h*
α-Bromopropionic acid	2300	400	2·6	0·006	$>C-Br$	$n \rightarrow \sigma$	*i*
L-Cystine	2500	300	0·7	0·002	$-S-S-$	$n \rightarrow \sigma$	*g*

References: (*a*) Ballard and Mason, *J.*, 1963, 1624. (*b*) Lowry and Hudson, *Phil. Trans.*, 1933, *A*, **232**, 117. (*c*) Mitchell and Gordon, *J.*, 1936, 853. (*d*) Mitchell and Simpson, *J.*, 1940, 784. (*e*) Kuhn and Lehmann, *Z. phys. Chem.*, 1932, *B*, **18**, 32. (*f*) *Idem, Z. Elektrochem.*, 1931, **37**, 549. (*g*) Ballard and Mason, unpublished result. (*h*) Kuhn, *Z. phys. Chem.*, 1935, *B*, **29**, 256. (*i*) Kuhn and Wolf, *Ber.*, 1930, **63**, 237.

In the original treatment[21] the $n \rightarrow \sigma$ transition of the carbonyl group was shown to consist largely of the oxygen $2p_y \rightarrow 2p_z$ atomic transition, which has a theoretical magnetic moment of $1{\cdot}0\beta_M$ in the x-direction. It was assumed that perturbations arising from the incomplete screening of the nuclei by the electrons of the 3-methyl group and the *cis*-4-hydrogen atom



(8)

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[57] Moscowitz, *Tetrahedron*, 1961, **13**, 48.

in the ketone (8) mixed the $n \rightarrow \sigma$ transition with a small component of the oxygen $2p_y \rightarrow 3d_{xy}$ atomic transition, which has an electric dipole moment in the required x-direction. The theoretical rotatory power of 3-methylcyclopentanone (8) obtained[21] upon this basis was of the same order of magnitude as that observed experimentally. In the equivalent analysis based upon the $n \rightarrow \pi$ assignment of the 3000 Å carbonyl absorption,[57] it is assumed that the rotatory power of saturated dissymmetric ketones arises from the mixing of the oxygen $2p_y \rightarrow 2p_x$ and $2p_y \rightarrow 3d_{yz}$ atomic transitions, which have, respectively, a magnetic and an electric moment directed along the carbonyl bond axis

Vol'kenshtein and Kruchek[58] have, however, pointed out recently that the Slater orbitals used by Kauzmann *et al.*[21] are somewhat too large, the oxygen $2p$-orbitals employed having charge density maxima at 1·41 Å from the oxygen nucleus, whereas the experimental carbonyl bond length[59] is only 1·21 Å. Repeating the calculation of the rotatory power of 3-methylcyclopentanone (8) with the atomic orbitals of carbon and oxygen given by Pople and Sidman[60] for formaldehyde, Vol'kenshtein and Kruchek showed[58] that the earlier estimate[21] was too large by a factor of 10^4.

Moreover, the lowest $2p \rightarrow 3d$ transition of oxygen lies experimentally[61] at 97,420 cm.$^{-1}$ (1027 Å). whereas a theoretical value only 36,000 cm.$^{-1}$ above the energy of the 3000 Å carbonyl absorption was employed in the early study.[21] Thus the degree to which the two transitions mix was overestimated, for, other factors being equal, the extent of the borrowing of dipole strength is inversely proportional to the square of the separation between the two transition energies.[62] Between 1000 and 3000 Å it is probable that there are a number of electronic transitions which mix more extensively than the oxygen $2p \rightarrow 3d$ excitation with the $n \rightarrow \pi$ transition of carbonyl compounds.

Studies[63–66] of the effects of substituents upon the intensity of the 3000 Å carbonyl absorption suggest that the most important of these donor transitions has a charge-transfer character. The extinction coefficient of the formaldehyde $n \rightarrow \pi$ band ($\epsilon_{\text{max.}} = 5$) is doubled and then quadrupled on the progressive replacement of hydrogen atoms by methyl groups, and grosser intensity changes result from the substitution of formally non-conjugated unsaturated groups (Table 3), or of atoms bearing lone-pair electrons (Table 4), at positions vicinal to the carbonyl group along a saturated carbon chain.

The absorption spectra of such substituted ketones often contain

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[58] Vol'kenshtein and Kruchek, *Optics and Spectroscopy*, 1960, **9**, 243.
[59] Lawrence and Strandberg, *Phys. Rev.*, 1951, **83**, 363.
[60] Pople and Sidman, *J. Chem. Phys.*, 1957, **27**, 1270.
[61] Moore, Nat. Bur. Standards (U.S.) Circ. No. 467, 1949.
[62] Herzberg and Teller, *Z. phys. Chem.*, 1933, *B*, **21**, 410.
[63] Cookson, *J.*, 1954, 282.
[64] Cookson and Wariyar, *J.*, 1956, 2302.
[65] Cookson and MacKenzie, *Proc. Chem. Soc.*, 1961, 423.
[66] Cookson and Hudec, *J.*, 1962, 429.

bands which can be ascribed to neither of the chromophores separately. A number of $\beta\gamma$-unsaturated ketones absorb, with various intensities, in the 2000—2600 Å region (Table 3) between the 1800 Å olefin absorption and the 3000 Å carbonyl band. In the same region occur the high-intensity bands of $\alpha\beta$-unsaturated ketones, due to a $\pi\rightarrow\pi$ transition which is known to have a charge transfer character,[67] and the corresponding transition may occur with a reduced probability in a $\beta\gamma$-unsaturated ketone if the π-orbitals of the carbonyl and the vinyl group overlap or are quasiconjugated.

TABLE 3. *Electronic spectra and circular dichroism of unsaturated ketones.*

Compound	Absorption		Circular dichroism		Ref.	
	$\lambda_{max.}$ (Å)	ϵ	$\lambda_{max.}$ (Å)	$(\epsilon_l—\epsilon_r)$	Absn.	Dich.
Bicyclo[2,2,2]oct-5-en-2-one (5)	2980 2020	110 3000	2980	10·1	53	*j*
Bicyclo[2,2,1]hept-5-en-2-one	3080 2100	290 3000	3060 <2400	9·6 <1	53	*j*
Parasantonide (7)	3080 2280	805 6600	3070 <2400	29·5 <-5	*j*	*j*
Dimethyldibenzosuberone (14)	2975 2450	670 9800	3000 2550	33 29	*j*	*j*
(−)-Carvone	3285 2290	33 10,000	3275 2300	0·22 2·5	*g*	*g*
(+)-Pulegone	3290 2460	34 5600	3330 <2600	0·33 $<-0·1$	*g*	*g*
3β-Hydroxy-androst-5-en-17-one	2940 2395	46 70	2990 2360	2·95 −0·2	*g*	*g*
5α-Androst-2-en-17-one	2960 2355	40 101	2985 2340	3·45 −0·3	*g*	*g*
Androsta-3,5-dien-17-one	2930 2360	131 22,400	2990 2300	2·99 -10^2	*g*	*g*

References: (*g*) See Table 2. (*j*) Bunnenberg, Djerassi, Mislow, and Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 2823.

A theoretical study[53] has shown that the π-overlap between the carbonyl and the vinyl group of bicyclo[2,2,2]oct-5-en-2-one (5) is about one-quarter of that between the corresponding groups of an unhindered $\alpha\beta$-unsaturated ketone, and the moment calculated for the charge-transfer transition of an electron from the vinyl bonding π-orbital to the carbonyl antibonding π-orbital accounts quantitatively for the absorption intensity

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[67] Kosower and Remy, *Tetrahedron*, 1959, **5**, 281.

of the band at 2020 Å (Table 3). The enhancement of the 3000 Å carbonyl absorption of the ketone (5) was ascribed to the mixing of the $n \rightarrow \pi$ with the charge-transfer $\pi \rightarrow \pi$ transition, due to the overlap between the oxygen lone-pair orbital and the π-orbital of the vinyl group allowed by the non-coplanar stereochemistry of the unsaturated groups in the molecule.

TABLE 4. *Wavelength* ($\lambda_{max.}$) *and the extinction coefficient* (ϵ) *of the* 3000 Å *absorption, and the wavelengths of the peak* (λ_{peak}) *and the trough* (λ_{trough}), *together with the amplitude* $[A]$ *of the molecular rotation anomaly in the optical rotatory dispersion curve, of some steroidal ketones substituted at a carbon atom vicinal to the carbonyl group* (*ax* = *axial, eq* = *equatorial substitution*).

Compound	Substn.	$\lambda_{max.}$ (Å)	ϵ	λ_{peak}	λ_{trough}	$[{}_aA_g]$	Refs.	
							absn.	rotn.
5α-Cholestan-2-one		2795	25	3100	2670	12,100°	*k*	*l*
3α-Bromo- ,,	*ax*	3120	110	3350‡	2900‡	27,200‡	*k*	*m*
3α-Phenyl- ,,	*ax*	2990	220	3170	2800	30,300	66	66
3β-Phenyl- ,,	*eq*	2820	60	3170	~2750	~4800	66	66
5α-Cholestan-3-one		2860	23	3070	2670	6570	63	*m*
2α-Fluoro- ,,	*eq*	2800	18	3090	2600	4810	*n*	*n*
2α-Chloro- ,,	*eq*	2790	40	3100	2650	5400	63	*n*
2α-Bromo- ,,	*eq*	2820	39	3100	2700	6200	63	*n*
2,2′-Dibromo- ,,	*ax*+*eq*	2940	135	3300	2900	18,600	63	*m*
3β-Acetoxy-5α-cholestan-7-one		2830	56	2740	3100	−1500	63	*m*
6±-Bromo- ,,	*eq*	2790	72	2650	3000	−2700	63	*m*
6β-Bromo- ,,	*ax*	3090	182	3350	2875	14,300	63	*m*
8β-Bromo- ,,	*ax*	3040*	158*	2875	3350	−30,900	63	*m*
3β-Acetoxy-5α-spirostan-11-one		2940	55	3250	<2900	⩾1500	63	*m*
12α-Fluoro- ,,	*ax*	3100	†	3400	2900	11,700	*m*	*m*
12α-Chloro- ,,	*ax*	3100	†	2900	3400	−11,600	*m*	*m*
12α,23-Dibromo- ,,	*ax*	3170	195	3000	3400	−14,800	63	*m*

* Values for the corresponding 6α,8β-dibromo-compound. † Values not recorded. ‡ Values for 3α-bromo-17β-propionyloxy-5α-androstan-2-one.

References: (*k*) Cookson and Dandegaonker, *J.*, 1955, 352. (*l*) Djerassi, Closson, and Lippman, *J. Amer. Chem. Soc.*, 1956, **78**, 3163. (*m*) Djerassi, Osiecki, Riniker, and Riniker, *ibid.*, 1958, **80**, 1216. (*n*) Djerassi, Fornaguera, and Mancera, *ibid.*, 1959, **81**, 2383.

Slater orbitals at large internuclear separations are unreliable, and it is doubtful whether the calculated overlap (0·0021) between the oxygen lone-pair and the vinyl π-orbital[53] in the ketone (5) is physically meaningful. Moreover, the overlap postulated cannot account generally for the phenomenon, since a charge-transfer band and the enhancement of the 3000 Å carbonyl absorption intensity are observed in cases, such as

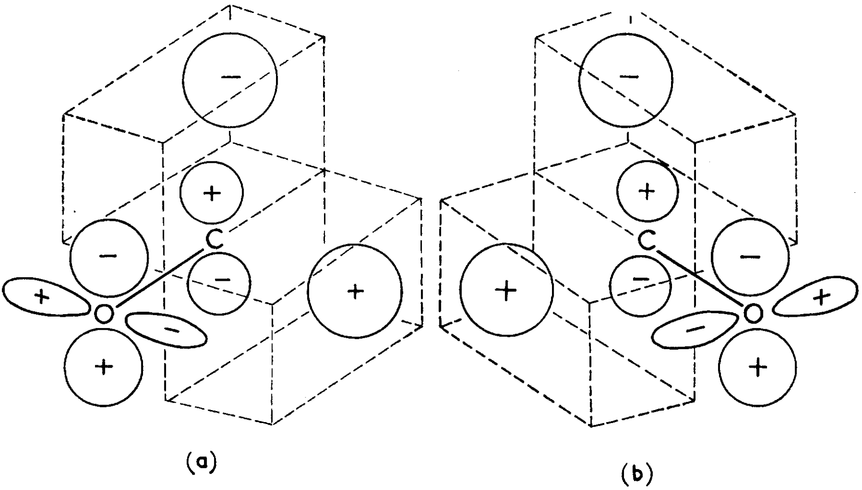
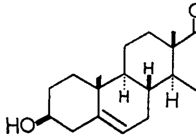


FIG. 7. *The relative positions and phases of the orbitals involved* (*eqns.* 31 *and* 32) *in the electronic transition responsible for the* 3000 Å *absorption of an optically active ketone with* (*a*) *an electron-donating substituent in the lower-right or upper-left rear octant, or with two such substituents, one in each of these octants, and* (*b*) *an electron-donating substituent in the upper-right or lower-left rear octant, or with two such substituents, one in each of these octants.*

dehydroisoandrosterone (9) (Table 3, Fig. 7), where the carbonyl and the vinyl group are separated by some 8 Å. In general, it appears probable that the lone-pair electrons of the carbonyl-oxygen atom are delocalised in all ketones, although the major portion of the lone-pair charge density is located upon the oxygen atom, and the charge densities upon the carbon atoms are small. The carbonyl antibonding π-orbital is similarly extended, and in unsaturated ketones, such as (5) and (9), the vinyl group is weakly conjugated through the saturated carbon atoms with the lone-pair and the antibonding π-orbital of the carbonyl group. On this view the mixing of the $n \rightarrow \pi$ and the charge-transfer $\pi \rightarrow \pi$ transitions in non-planar unsaturated ketones is due to the overlap between successive pairs of orbitals on adjacent atoms linking the carbonyl and the vinyl group, and not to the direct overlap of the carbonyl lone-pair and antibonding π-orbital with the vinyl π-orbitals.



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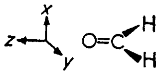

(10)

The delocalisation of the carbonyl lone-pair electrons is apparent from recent self-consistent field treatments of formaldehyde.[68,69] The forms of

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[68] Goodfriend, Birss, and Duncan, *Rev. Mod. Phys.*, 1960, **32**, 307.

[69] Foster and Boys, *Rev. Mod. Phys.*, 1960, **32**, 303.

the highest occupied and the lowest unoccupied orbitals, ψ_1 and ψ_2 respectively, are[68]

$$\psi_1 = 0{\cdot}905 Y_{\mathrm{O}} - 0{\cdot}270 Y_{\mathrm{C}} - 0{\cdot}299(\mathrm{H}_1 - \mathrm{H}_2), \tag{29}$$

and $$\psi_2 = 0{\cdot}812 X_{\mathrm{O}} - 0{\cdot}779 X_{\mathrm{C}}, \tag{30}$$

where Y_{O} and Y_{C} refer to the $2p_y$-orbitals of oxygen and carbon, respectively, and X_{O} and X_{C} to the corresponding $2p_x$-orbitals, with H_1 and H_2 representing hydrogen $1s$ orbitals, the co-ordinates being as in (10). The form of the highest-energy occupied orbital of formaldehyde, ψ_1 (eqn. 29), indicates that a substantial portion of the charge density is located upon the methylene group, and a similar treatment of more complex carbonyl compounds would probably reveal an analogous delocalisation of the oxygen lone-pair electrons. Since part of the lone-pair charge density is located upon the methylene group, the $n \rightarrow \pi$ transition of formaldehyde, $\psi_1 \rightarrow \psi_2$, involves the transfer of charge from the hydrogen atoms to the carbonyl antibonding π-orbital. The charge-transfer component of the $\psi_1 \rightarrow \psi_2$ transition becomes electric dipole allowed with y-polarization when the molecule is at, or near to, the turning points of the vibration which carries the hydrogen atoms above or below the molecular yz-plane (10), whereas the magnetic dipole component is z-polarized, the moment calculated[52] from eqns. (29) and (30) being $1{\cdot}1\beta_{\mathrm{M}}$.

The enhanced intensity of the 3000 Å absorption observed on replacing the hydrogen atoms of formaldehyde by alkyl groups may be ascribed to an increased contribution to the absorption from the charge-transfer transition. Paraffins, no less than olefins, ethers, and other lone-pair donors, give charge-transfer absorption bands with iodine,[70] the ionisation potentials of paraffins being only 0·9—1·1 ev higher than those of the corresponding olefins.[71] Perfluoroalkyl groups are poor electron-donors, however, and the intensity of the $n \rightarrow \pi$ band of acetone[72] ($\epsilon_{\mathrm{max.}}$ 22) is reduced in the corresponding trifluoro-derivative[73] ($\epsilon_{\mathrm{max.}}$ 9). The perfluoroparaffins give no charge transfer absorption with iodine,[70] and trifluoromethane[74] has a higher ionisation potential (13·8 ev) than methane[71] (12·99 ev).

An electron-donating substituent which enhances the 3000 Å absorption intensity of an optically active ketone frequently augments the rotatory power of the compound.[64,75] In dissymmetric cyclohexanones both the intensity enhancement of the 3000 Å absorption[63] and the change in rotatory power[66,76] depend critically upon the stereochemical orientation

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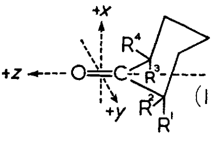
[70] Evans, *J. Chem. Phys.*, 1955, **23**, 1424, 1426.
[71] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.
[72] Stich, Rotzler, and Reichstein, *Helv. Chim. Acta*, 1959, **42**, 1480.
[73] Smith and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 2345.
[74] Stokes and Duncan, *J. Amer. Chem. Soc.*, 1958, **80**, 6177.
[75] Woodward and Kovach, *J. Amer. Chem. Soc.*, 1950, **72**, 1009.
[76] Djerassi and Klyne, *J. Amer. Chem. Soc.*, 1957, **79**, 1506.

of the substituent. When placed on either of the carbon atoms adjacent to the carbonyl group in cyclohexanone, an equatorial halogen atom or phenyl group (11; R^2 or R^4 = the substituent, the remaining R's = H)

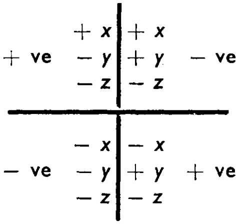


(11)

produces only small changes in the intensity of the 3000 Å absorption and in the rotatory power of the molecule, whereas the changes induced by a corresponding axial halogen or phenyl group (11; R^1 or R^3 = the substituent, the remaining R's = H) are large (Table 4).

The two isomeric axial α-halogenocyclohexanones are distinguished by rotatory power changes, due to the substituent, of opposite sign.[76] A chlorine or bromine atom replacing a hydrogen atom at R^1 in the ketone (11) enhances the absorption of left-circularly polarized light, conferring a positive rotational strength upon the band, whereas the absorption of right-circularly polarized light is differentially favoured if the halogen atom is substituted at R^3 (Table 4). An axial bromine atom produces a larger change of rotatory power than a corresponding chlorine atom, and an axial fluorine atom substituted at the same α-position induces a rotatory power change of opposite sign (Table 4).

These observations provide the basis for the octant rule,[42] which relates the sign of the rotatory power of an optically active ketone in the 3000 Å region to the stereochemical disposition of the atoms conferring dissymmetry upon the molecule. The nodal planes of the oxygen $2p_y$ lone-pair and the carbonyl antibonding π_x orbital (11) divide the molecular environment of the carbonyl group into eight spatial regions, of which the four rear octants in the $-z$ hemisphere are generally the more important. A group or an atom, other than fluorine, placed in the upper-left or the lower-right rear octant (12), relative to an observer viewing the molecule in the $-z$ direction (11), induces a positive rotatory power in the molecule at 3000 Å, whereas a negative rotatory power is produced by the corresponding substitution in the upper-right or lower-left rear octant (12).



(12)

Substitution by fluorine induces a change in the rotatory power of opposite sign to that given by a corresponding alkyl or unsaturated group, or any of the other halogen atoms.[42,66,76,77] Being a poor electron-donor, the fluorine atom makes a smaller charge-transfer contribution to the $n\rightarrow\pi$ transition than does the hydrogen atom which it replaces, and the 3000 Å absorption intensity is reduced (Table 4). In compound (11; R's = H) the electric moments of the charge-transfer contributions from the hydrogen atoms, R^1 = H and R^3 = H, have components in the z-direction which are of equal magnitude and antiparallel, giving a net rotational strength of zero, but if R^1 = F the contribution of the remaining hydrogen atom, R^3 = H, dominates, and the compound (11; R^1 = F, $R^2 = R^3 = R^4$ = H) has a net negative rotational strength, as have the cyclohexanones with an R^3 substituent which is a stronger electron donor than hydrogen.

Groups occupying a position in, or close to, a nodal plane, such as the halogen atom in α-equatorial halogenocyclohexanones (11; R^2 or R^4 = halogen, the remaining R's = H) produce only a small change in the rotatory power and in the intensity of the 3000 Å absorption (Table 4) since the lone-pair orbitals of the halogen atom cannot overlap simultaneously the oxygen $2p_y$ lone-pair and the carbonyl antibonding π_x-orbital, except at nuclear positions near to the turning points of the vibration which carries the halogen atom into the octants above and below the yz-plane. The mixing of the charge-transfer transition of a halogen lone-pair electron with the carbonyl antibonding π-orbital is vibrationally induced and small in the equatorial α-halogenocyclohexanones, but in the axial isomers the mixing is more extensive, as the halogen lone-pair orbitals overlap the oxygen $2p_y$ lone-pair and the carbonyl antibonding π_x-orbital simultaneously when the halogen atom lies at its equilibrium nuclear position.

Including the charge-transfer interaction, the 3000 Å absorption of substituted ketones may be ascribed to a transition between the composite orbitals,

$$\psi_3 = 2p_y - c_1D, \qquad (31)$$

and

$$\psi_4 = \pi_x{}^* - c_2D, \qquad (32)$$

where $2p_y$, $\pi_x{}^*$, and D refer, respectively, to the oxygen $2p$ lone-pair orbital, the carbonyl antibonding π-orbital, and the donor orbital of the substituent, the mixing coefficients, c_1 and c_2, being small compared with unity. The orbitals of the atoms composing the carbon chain which links the carbonyl group to the donor substituent contribute to ψ_3 and ψ_4, the coefficients being very small and of undetermined sign. On spectroscopic grounds, ψ_3 and ψ_4 should represent negative, antibonding, combinations of the orbitals making the major contributions (eqns. 31 and 32). In equatorial α-halogenocyclohexanones and, more particularly, in the acetyl halides, the carbonyl $n\rightarrow\pi$ band is shifted to shorter wavelengths by the halogen atom,[63] suggesting that the energy of the carbonyl antibonding

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[77] Moscowitz, Mislow, Glass, and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1945.

π-orbital is raised by the substituent. A converse shift of the carbonyl $n \to \pi$ band to longer wavelengths is observed[63] in the axial α-halogenocyclohexanones, where the substituent overlaps both the oxygen lone-pair and the carbonyl π-orbital, indicating that the energy of the oxygen lone-pair orbital is raised even more than that of the carbonyl antibonding π-orbital by the halogen atom.

In a dissymmetric ketone with a donor group in the lower-right or the upper-left rear octant, or with donor groups in both of these octants, the relative positions and phases of the orbitals involved in the transition $\psi_3 \to \psi_4$ (Fig. 7a) give the electric dipole moment of the charge transfer contribution a component directed parallel to the magnetic moment, orientated along the carbonyl bond direction, and the transition has a positive rotational strength. In the enantiomer, with donor groups in the upper-right or lower-left rear octant, or in both of these octants (Fig. 7b), the component excitation, $2p_y \to 2p_x$, at the oxygen atom involves a rotatory displacement of charge in the opposite sense, and the resultant magnetic moment is then antiparallel to the component of the charge-transfer electric moment directed along the carbonyl bond axis, giving the transition $\psi_3 \to \psi_4$ of the enantiomer a negative rotational strength.[52]

The model used by Labhart and Wagniere[53] to explain the absorption spectrum of bicyclo[2,2,2]oct-5-en-2-one (5) has been extended recently[77] to account for the rotatory powers of the two enantiomers of the molecule at 3000 Å. The positive rotational strength of this compound at 3000 Å is ascribed to the transition $\psi_5 \to \psi_6$, where

$$\psi_5 = 2p_y + c_1 D, \tag{33}$$

and

$$\psi_6 = \pi_x^* + c_2 D, \tag{34}$$

and the negative rotational strength of the enantiomer of form (5) is attributed[77] to the transition $\psi_3 \to \psi_6$. The molecular orbital, ψ_5, represents a bonding combination of the oxygen lone-pair and the donor orbital, and ψ_5 has a lower energy than the antibonding combination, ψ_3, implying that compound (5) should absorb at a shorter wavelength than its enantiomer. However, the absorption spectra of the optical isomers of a given compound, measured with unpolarized light, are invariably identical.

The mixing of the electronic excitations requires that the charge-transfer transition of substituted ketones contains a small contribution from the carbonyl $n \to \pi$ transition. The charge-transfer absorption of formally non-conjugated unsaturated ketones may be attributed to the transition $\psi_7 \to \psi_4$, where

$$\psi_7 = D + c_1 2p_y. \tag{35}$$

Representing a bonding combination, ψ_7 lies below ψ_3 in energy, in accord with the observed positions of the charge transfer and $n \to \pi$ bands of unsaturated ketones (Table 3). If the charge-transfer transition has no magnetic moment, the rotational strengths of the $n\rightarrow\pi$ and the charge-transfer absorption band should have equal magnitudes, but opposite signs, eqns. (18), (31), (32), and (35) giving

$$R_{\text{C.T.}} = -R_{n\rightarrow\pi} = c_1\mu_{n\rightarrow\pi}\,p_{\text{C.T.}}\cdot\cos\theta, \tag{36}$$

where C.T. and $n\rightarrow\pi$ refer to the charge-transfer and $n\rightarrow\pi$ transition, respectively.

Dissymmetric unsaturated ketones which are formally non-conjugated commonly give $n\rightarrow\pi$ and charge-transfer absorption bands with rotational strengths of opposite sign (Fig. 8, Table 3), but exceptions have been observed,[78] *e.g.*, compound (6), and the rotational strength of the charge-transfer band is generally smaller than that of the $n\rightarrow\pi$ absorption (Table 3). These observations suggest that the charge-transfer transition involves, in general, a rotatory as well as a translatory displacement of charge, the intrinsic rotational strength of the charge transfer having a sign opposite to that of the rotational strength acquired by the admixture of a small contribution from the $n\rightarrow\pi$ transition. The steric disposition of the donor orbitals (Fig. 7) requires a rotatory and a translatory displacement of charge in the charge-transfer transition, the magnetic moments of the $n\rightarrow\pi$ and the charge-transfer transition being parallel for the 3000 Å absorption (eqns. 31 and 32) and antiparallel for the charge-transfer absorption (eqns. 32 and 35).

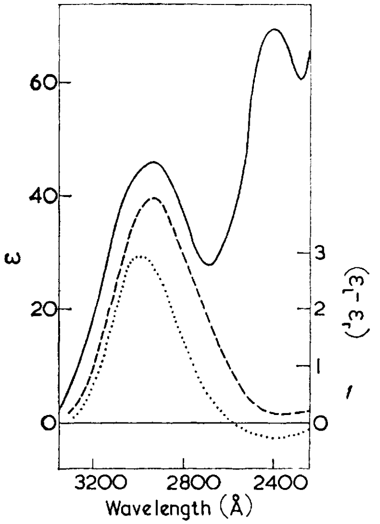

FIG. 8. *The circular dichroism* (........) *and the absorption spectrum* (——) *of dehydroepiandrosterone* (9), *and the absorption spectrum* (----) *of epiandrosterone* (15), *in ethanol.*

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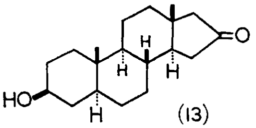
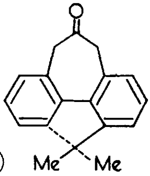
[78] Bunnenberg, Djerassi, Mislow, and Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 2823.

The observed rotational and dipole strengths of the 3000 Å absorption given by dissymmetric ketones with C_2 symmetry give an experimental value for the magnetic dipole moment of the carbonyl $n \rightarrow \pi$ transition.[52] The immediate molecular environment of the carbonyl group in the 16-keto-steroid (13), namely, the atoms of rings C and D, approximates to the C_2 symmetry of the ketone (2), the atoms of rings A and B being too far distant from the carbonyl group to have a significant influence upon the chromophore. The total dipole strength of the 3000 Å absorption band given by the steroid (13), 575×10^{-40} c.g.s., may be divided into two components, one directed perpendicular and the other parallel to the carbonyl bond axis. The perpendicular component is given approximately by the dipole strength of the corresponding absorption of the inactive parent ketone, 258×10^{-40} c.g.s., obtained from the 3000 Å band area of cyclopentanone, and the difference, 317×10^{-40} c.g.s., is then the dipole strength of the carbonyl absorption given by compound (13) oriented parallel to the carbonyl bond axis. The experimental rotational strength of the 3000 Å absorption of the steroid (13) is $16{\cdot}7 \times 10^{-40}$ c.g.s., whence the magnetic moment of the $n \rightarrow \pi$ transition is $1{\cdot}0\beta_M$. The same value has been obtained[52] from the absorption and optical rotatory dispersion data[77] for the dimethyl-dibenzosuberone (14) in the 3000 Å region.



(13)

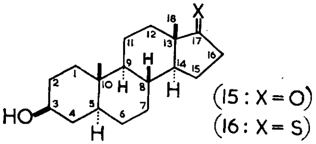


(14)

Since the same value for the magnetic moment is given by ketones of such widely differing types as (13) and (14), it is probable that the magnetic moment is approximately constant in the $n \rightarrow \pi$ transition of ketones generally. In dissymmetric ketones lacking an element of symmetry, the angle, θ (eqn. 18), may be derived from the experimental rotational and dipole strengths of the 3000 Å absorption by using the value, $\mu = 1{\cdot}0\beta_M$. For the 17-keto-steroid (15), the observed[79] rotational and dipole strengths of the $n \rightarrow \pi$ band are 8·2 and 520, respectively, in units of 10^{-40} c.g.s., giving the value, $\theta = 67°$, for the angle between the directions of the electric and the magnetic moments of the transition. The gross electric moment, making an angle of 67° to the carbonyl bond at the origin of the co-ordinates defining the octants, is the vector sum of a number of contributions. The contribution from ring D, directed perpendicular to the carbonyl bond, is given by the data for cyclopentanone ($D = 258 \times 10^{-40}$ c.g.s.), so that approximately one half of the dipole strength of the 3000 Å absorption given by compound (15) is contributed by the substituents of ring D, namely, the atoms of rings A, B, and C, and the 18-methyl group.

[79] Ballard and Mason, *J.*, 1963, 1624.

The vector joining the 18-methyl group of the 17-keto-steroid (15) to the origin makes an angle of ~30° with the carbonyl bond, and, according to the octant rule,[42] this group confers upon the $n \rightarrow \pi$ transition of compound (15) an electric moment with a component antiparallel to the magnetic moment, contributing a rotational strength of negative sign. The vectors joining the atoms of rings A, B, and C to the origin are orientated at an average angle of ~45° to the carbonyl bond, and these atoms confer a larger electric moment, which has a component parallel to the magnetic moment, so that the net rotational strength of the $n \rightarrow \pi$ band given by the ketone (15) is positive in sign. The particular angles between the carbonyl bond and the vectors joining the origin to the substituents of ring D, estimated from a model, and the relative phases of the electric moments originating from those substituents, determined by the octant rule,[42] account for the experimentally estimated angle, $\theta = 67°$, if the total dipole strength of the 3000 Å absorption of the 17-keto-steroid (15) is made up from the following contributions, in units of 10^{-40} c.g.s.: 260 from ring D, 245 from rings A, B, and C, and 15 from the 18-methyl group.[79]



(15 : X = O)
(16 : X = S)

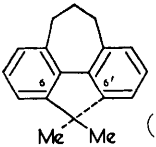
The particular values of the contributions are not important, for they cannot be at all precise, but the relative magnitudes are significant. A notable feature is the small contribution to the dipole strength from the 18-methyl group compared with that from the atoms of rings A, B, and C, for of the latter only the 12-methylene group is as close to the carbonyl bond as the 18-methyl group, and any contribution should fall off rapidly in a saturated molecule as the distance between the interacting groups is increased, although the contribution may be detected at large separations, *e.g.*, compound (9) (Fig. 8).

In general, the ionisation potentials of alkanes lie in the order, primary > secondary > tertiary > quaternary, relevant values[71] being 11·65 ev for ethane and 9·88 ev for cyclohexane. Thus the charge-transfer transition of an electron from the 18-methyl group to the carbonyl antibonding π-orbital of the ketone (15) occurs at a higher energy than the corresponding transitions from the 12-methylene group and the other atoms of rings A, B, and C. Consequently, the charge-transfer transition from the 18-methyl group mixes less with the carbonyl $n \rightarrow \pi$ transition, and it makes only a small contribution to the dipole strength of the 3000 Å absorption of the steroid (15).

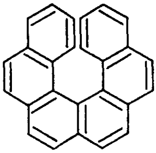
The estimated angle, $\theta = 67°$, for the 3000 Å absorption of the ketone (15) may be used further to obtain[79] a value for the magnetic moment of the 5000 Å absorption of the corresponding thioketone (16). Although

17-thiocarbonyl steroids have been prepared, attempts[80] to synthesise 16-thione analogues have not been successful as yet, and the direct method used[52] to estimate the magnetic moment of the carbonyl $n \rightarrow \pi$ transition cannot be employed for the corresponding thiocarbonyl transition. However, if it is assumed that the same angle between the electric moment and the magnetic moment obtains in the $n \rightarrow \pi$ transition of the ketone (15) and the corresponding thioketone (16), the experimental[79] rotational and dipole strengths of the 5000 Å absorption of the latter, 3·0 and 180, respectively, in units of 10^{-40} c.g.s., give a magnetic moment of $0{\cdot}62\beta_M$ for the thiocarbonyl $n \rightarrow \pi$ transition.

Helical Conjugated Molecules.—The optical rotatory power of the high-intensity absorption bands given by a conjugated molecule arises in general from electric dipole transitions in a π-electron system which is sterically distorted into a helical configuration. A steric constraint applied to a conjugated molecule may be relieved either by the torsion of a readily deformable bond, such as the internuclear bond of a biaryl compound, *e.g.*, (17), or by the uniform distribution of the steric strain throughout the molecule, as in the case of the overcrowded aromatic hydrocarbons, *e.g.*, (18). To these two modes of deformation correspond two mechanisms whereby an electric dipole $\pi \rightarrow \pi$ transition acquires a magnetic moment and a rotational strength.



(17)


(18)

If a carbon–carbon double bond is twisted (Fig. 9), the nodal planes of the carbon $2p_\pi$-orbitals no longer coincide, and the $\pi \rightarrow \pi$ transition involves a rotatory and a translatory displacement of charge, giving a rotational strength directed along the carbon–carbon bond. The dipole and the rotational strengths of the transition are related to the angle of twist, β, by

$$D = D_{\max.}\cos^2 \beta, \tag{37}$$

$$\text{and } R = R_{\max.}\sin 2\beta. \tag{38}$$

For a given $\pi \rightarrow \pi$ transition of a molecule in which the steric strain is uniformly distributed, the rotational strength is made up by contributions from each individual bond, but in a hindered biphenyl (Fig. 9), on the assumption that each benzene ring retains its plane, the torsion of the internuclear bond contributes a rotational strength only to the transitions

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[80] Djerassi and Herbst, *J. Org. Chem.*, 1961, **26**, 4675.

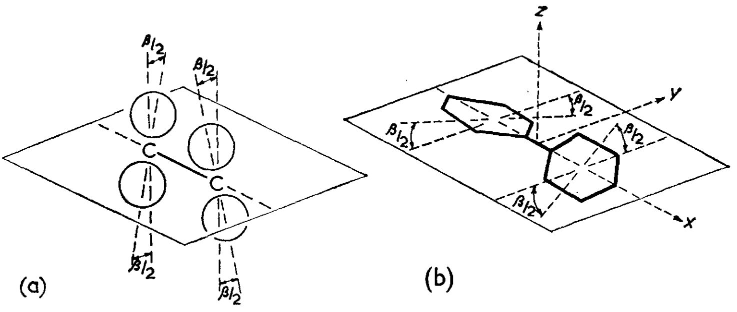
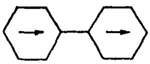
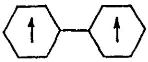


FIG. 9. *Distorted π-electron systems: (a) a carbon–carbon double bond twisted through an angle, β, and (b) a biaryl compound with an angle, β, between the planes of the aromatic rings.*

which are polarized in the direction of the long axis of the molecule (19), indeed, the rotational strength of such a transition is provided entirely by the local moments along the twisted bond. The local electric moment along the internuclear bond of biphenyl is only a small fraction of the total electric moment of any long-axis polarized transition (19), and the rotational strengths of these transitions should be very small in relation to the dipole strengths.


(19)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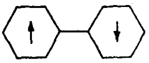
(21)

The π→π transitions of biphenyl which are polarized perpendicularly to the long axis, namely, those with the instaneous moments (20) and (21), attain a rotational strength in the non-planar molecule (Fig. 9) owing to the coupling of the partial electric moments of each aromatic nucleus. The partial moments, (20), parallel in the planar molecule, give a dipole and a rotational strength orientated in the *y*-direction (Fig. 9) in the twisted molecule, whereas the corresponding strengths given by the partial moments, (21), which are antiparallel in the planar molecule, are orientated in the *z*-direction (Fig. 9). As functions of the dihedral angle, β, between the planes of the aromatic rings of biphenyl, the rotational and dipole strengths are

$$R_z = -R_y = R_{\pi/2} \sin \beta, \tag{39}$$

$$D_z = D_0(1 - \cos \beta)/2, \tag{40}$$

$$D_y = D_0(1 + \cos \beta)/2. \tag{41}$$

The partial electric moments, (20) and (21), make up the total electric moment in each case, and the rotational strengths of the short-axis polarized transition of biphenyl should be larger than those of long-axis polarized transitions with similar dipole strengths.

Biphenyl is an inherently dissymmetric molecule,[81] having the symmetry D_2 for all non-zero angles of twist except $\pi/2$, where the molecule acquires two planes of symmetry and a four-fold rotation-reflection axis, belonging to the group D_{2d}. For the dihedral angle, $\beta = \pi/2$, the rotational strength of transitions with long-axis polarization vanishes (eqn. 38), and each short-axis polarized excitation of the now unconjugated benzene rings forms a symmetric (20) and an antisymmetric (21) combination, which are necessarily degenerate, so that the rotational strengths of the two resultant transitions mutually cancel (eqn. 39).

The Hückel molecular-orbital theory indicates that the long-wavelength absorption band of biphenyl is due to a transition which is long-axis polarized (19), and that the shorter-wavelength band in the quartz-ultraviolet region arises from a group of four transitions, degenerate in the zero order, which are short-axis polarized, one pair having the partial moments (20) and the other the moments (21). For angles of twist other than $\pi/2$ the degeneracy is split by electronic interactions.

The substituents required to give stable biphenyl enantiomers modify these polarization directions to some degree. In particular, the alkyl substituents of compound (17) confer electric moments with short-axis polarization upon the transition, giving the long-wavelength absorption band, as is shown (Fig. 10) by the appearance of two small circular dichroism bands[78] with comparable magnitudes but opposed signs in the 2800 Å region. The inherent rotational strength of a biphenyl transition with long-axis polarization would be manifest by a single circular

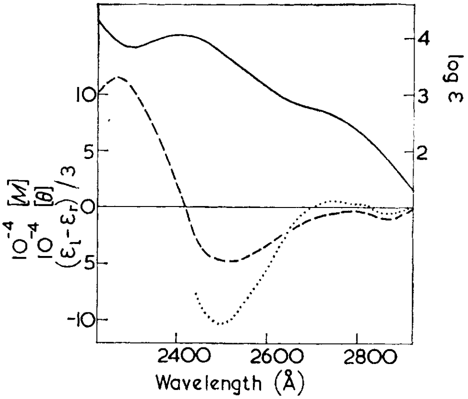

FIG. 10. *The circular dichroism (........), the optical rotatory dispersion (------), and the absorption spectrum (——) of the* (+)-*biphenyl* (17) *in iso-octane* (*based on data recorded in refs.* 78 *and* 81).

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[81] Mislow, Glass, O'Brien, Rutkln, Steinberg, Weiss, and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455.

dichroism band (eqn. 38), but the short-axis moments induced by the substituents form the combinations (20) and (21), giving (eqn. 39) the observed dichroism (Fig. 10). Thus the sign of the long-wavelength circular dichroism and optical rotatory dispersion of a substituted biphenyl should be determined primarily by the chemical nature of the substituents and not by the absolute configuration of the biphenyl nucleus, in agreement with the observation[81] that, for 2,2′-bridged biphenyls having the absolute (*S*)-configuration of (17), the sign of the long-wavelength Cotton effect is positive for 6,6′-dinitro-analogue, and negative for 6,6′-dimethyl- and the 6,6′-dichloro-derivative.

The circular dichroism absorption at 2500 Å (Fig. 10) under the shorter-wavelength absorption band of compound (17) has a larger rotational strength, supporting the polarization assignment of the Huckel theory, and the optical rotatory dispersion curve[81] indicates (Fig. 10) the presence of a complementary circular dichroism absorption at shorter wavelengths with a comparable magnitude and an opposed sign, as required by eqn. (39). Having a short-axis polarization and large intrinsic rotational strengths, the transitions responsible for the shorter-wavelength absorption of biphenyl derivatives should give circular dichroism and optical rotatory dispersion curves with signs determined primarily by the absolute configuration of the biphenyl nucleus, the effect of the substituents being small, in agreement with the rule[81] that biphenyl derivatives with the absolute (*S*)-configuration of (17), and a dihedral angle of *ca.* 45°, have a negative Cotton effect with an amplitude of the order of 10^5 degrees centred at 2400—2500 Å, irrespective of the nature of the substituents.

The twisted double-bond model (Fig. 9) has been used in calculating the rotatory power of hexahelicene[57,82] and of steroid dienes.[83,84] The distortions of hexahelicene (phenanthro[3,4-*c*]phenanthrene) (18) from planarity were estimated[82] from the *X*-ray diffraction data[85] for pentahelicene dibenzo[*c*,*g*]phenanthrene), and the calculated rotatory power was found to be in good agreement with that observed in both the transparent[82] and the absorption[57] wavelength region. For the dissymmetric dienes, Dreiding[86] models were used to estimate the distortion from planarity, and in the case of (+)-*trans*-1,4,4a,8a-tetrahydro-4a-methylnaphthalene, where the rotatory dispersion was measured through the long-wavelength absorption band, the calculated rotatory power was found to be in satisfactory agreement with experiment.[84]

From the study of dissymmetric dienes the rule has been formulated[84] that cisoid dienes twisted in the sense of a right-handed helix (22) have a strong rotational strength, $\sim 25 \times 10^{-40}$ c.g.s. or greater, giving a positive Cotton effect in the region of the long-wavelength absorption band, namely,

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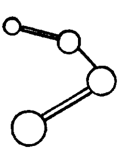
[82] Moscowitz, Thesis, Harvard University, 1957.
[83] Deen, Thesis, University of Leiden, 1961.
[84] Moscowitz, Charney, Weiss, and Ziffer, *J. Amer. Chem. Soc.*, 1961, **83**, 4661.
[85] McIntosh, Robertson, and Vand., *J.*, 1954, 1661.
[86] Dreiding, *Helv. Chim. Acta*, 1959, **42**, 1339.



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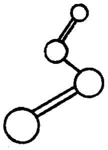

(23)

2600—2800 Å for polycyclic compounds. The rule has been extended[87] to $\alpha\beta$-unsaturated ketones, which, twisted in the sense of a right-handed helix in either the cisoid (22) or the transoid (23) conformation, give a strong positive Cotton effect in the region of the charge transfer $\pi \rightarrow \pi$ band at 2400—2600 Å.

Helical Polymers.—The optical rotatory power of macromolecules containing helically disposed unconjugated chromophores has been discussed recently in terms of coupled oscillator theory by Moffitt,[88] Fitts and Kirkwood,[89] and subsequent workers,[90] in connection with the alteration in optical rotation and rotatory dispersion observed[91] when polypeptides change from the random-coil to the α-helix conformation.

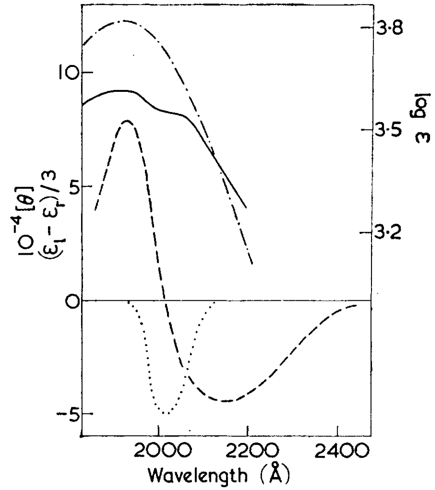

FIG. 11. *The circular dichroism (----) and the absorption spectrum (——) of the α-helix form of poly-*L*-glutamic acid, and the circular dichroism (........) and the absorption spectrum (-·—·—) of the random-coil form (based on data recorded in refs.* 92 *and* 100).

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[87] Djerassi, Records, Bunnenberg, Mislow, and Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 870.

[88] Moffitt, *J. Chem. Phys.*, 1956, **25**, 467; *Proc. Nat. Acad. Sci.*, 1956, **42**, 736.

[89] Fitts and Kirkwood, *Proc. Nat. Acad. Sci.*, 1956, **42**, 33; 1957, **43**, 1046.

[90] Tinoco, *Adv. Chem. Phys.*, 1962, **4**, 113; Tinoco and Woody, *J. Chem. Phys.*, 1960, **32**, 461; Schellman and Oriel, *ibid.*, 1962, **37**, 2114.

[91] Blout and Idelson, *J. Amer. Chem. Soc.*, 1956, **78**, 497; Doty and Yang, *ibid.*, 1956, **78**, 498.

The change in rotatory power is accompanied by a change in the absorption spectrum of the polypeptide[92] at 1900 Å (Fig. 11), both effects being due to the correlative interactions of the transition dipoles of the individual amide chromophores.

Moffitt considered[88] a helix composed of N amide residues, and he showed that of the N possible electronic transitions corresponding to a particular amide chromophore excitation, only three were allowed. The quasi-symmetric coupling of the individual amide chromophore excitations gives a transition with a moment directed along the axis of the helix (Fig. 12a), and two quasi-antisymmetric coupling modes give a degenerate transition with a moment directed perpendicular to the helix axis (Fig. 12b). Each of the allowed transitions involves a helical displacement of charge about the polarization direction, giving an electric and a magnetic dipole transition moment with the same orientation.

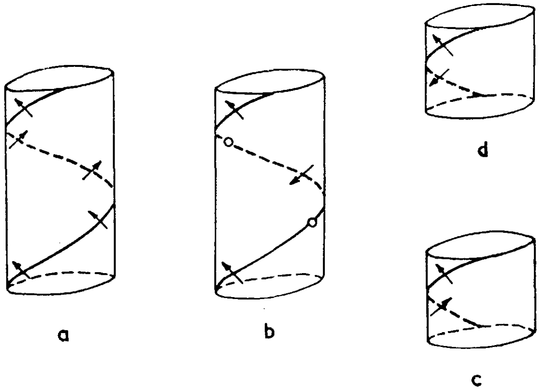

FIG. 12. *The transition moments in the polypeptide* α*-helix giving the* 1900 Å *amide absorption due to* (*a*) *the parallel, quasi-symmetric, coupling mode,* (*b*) *one component of the doubly degenerate, perpendicular, quasi-antisymmetric, coupling mode,* (*c*) *the quasi-symmetric coupling mode in a helical segment containing two amide residues, and* (*d*) *the quasi-antisymmetric coupling mode in a two-residue segment.*

For a right-handed helical polypeptide, and for a particular amide chromophore excitation with a dipole strength, D, and a frequency, ν, the resultant rotational strengths, per residue, of the transitions polarized parallel and perpendicular to the helix axis, $R_{\parallel}$ and $R_{\perp}$, respectively, are given by,[88]

$$R_{\parallel} = -R_{\perp} = \pi \nu d D \cos t \cos v, \tag{42}$$

where cos t and cos v are, respectively, the tangential and the vertical cosines of the transition moment vector in each individual amide chromophore, which lies at a radial distance, d, from the axis of the helix. The terms, vertical and tangential, refer to a cylindrical co-ordinate system, in

[92] Rosenheck and Doty, *Proc. Nat. Acad. Sci.*, 1961, **47**, 1775.

which the outward radial vector, the tangential vector, and the vertical direction of the advancing screw form a right-handed set of Cartesian axes (Fig. 13).

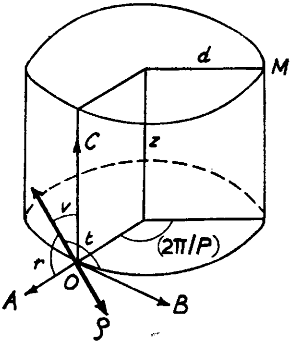

FIG. 13. *The orientation of the moment vector, ρ, of the π→π transition given by an amide residue at O in the cylindrical co-ordinate system of the α-helix, defined by the radial, tangential, and vertical vectors, OA, OB, and OC, respectively. The residue at M is related to that at O by the rise per residue along the helix axis, Z, and the angle about the helix axis (2π/P), where P is the number of amide residues per unit turn of the helix.*

If the radial cosine of the residue transition moment vectors is zero, as is probable for the π→π transitions of the amide chromophore in the α-helix since the planes of the amide groups are perpendicular to the radial vector from the helix axis,[93] the dipole strengths of the parallel and the perpendicular polarized transitions allowed in the α-helix stand in the ratio,

$$D_{\parallel}/D_{\perp} = \cos^2 v/\cos^2 t. \tag{43}$$

The transition with the smaller dipole strength gives rise to absorption at lower frequencies, the interval, $\Delta\nu$, between the energies of the two allowed transitions derived from a given amide group excitation being[88]

$$\Delta\nu = \nu_{\parallel} - \nu_{\perp} = \Sigma_m[1 - \cos(2\pi m/P)]V_m/\boldsymbol{hc} \tag{44}$$

where P is the number of amide residues per unit turn of the helix, and V_m is the energy of interaction between the instantaneous transition moments of a given residue and its neighbours, the summation being taken over all the neighbouring amide groups m.

Peptides and other amides give a broad π→π absorption band[94,95] near 1850 Å, with an oscillator strength of 0·27 ± 0·07 for peptides[94] and 0·237 for dimethylformamide.[95] Studies of the crystal spectrum of myristamide, measured with plane-polarized light,[96] indicate that the most probable orientation of the transition moment is at an angle of 9·1° to the nitrogen–

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[93] Pauling and Corey, *J. Amer. Chem. Soc.*, 1950, **72**, 5349; *Proc. Roy. Soc.*, 1953, *B*, **141**, 21.

[94] Ham and Platt, *J. Chem. Phys.*, 1952, **20**, 335.

[95] Hunt and Simpson, *J. Amer. Chem. Soc.*, 1953, **75**, 4540.

[96] Peterson and Simpson, *J. Amer. Chem. Soc.*, 1955, **77**, 3929.

oxygen direction, in the sense that a parallel line through the nitrogen atom cuts the carbonyl bond (Fig. 14). The α-helix[93,97] contains some 3·6 amide residues per unit turn, during which the helix, with a radius of 1·6 Å, rises through 5·4 Å. The disposition of a given amide group in the cylindrical co-ordinate system of a right-handed α-helix (Fig. 13) gives the direction of the transition moment responsible for the 1850 Å amide absorption vertical and tangential angles of some 50° and 140°, respectively.

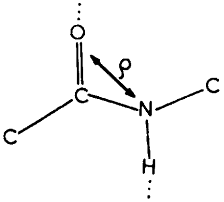

FIG. 14. *The orientation in the amide group of the transition moment, ρ, giving the 1900 Å polypeptide absorption.*

These values place the parallel-polarized transition of the α-helix at the lower frequency, Moffitt estimating[88] the energy separation (eqn. 44) to be $\Delta\nu = -2800$ cm.$^{-1}$. For the right-handed α-helix the degenerate perpendicular transition (Fig. 12b) should have a positive rotational strength with the value of $\sim 120 \times 10^{-40}$ c.g.s., whilst the parallel transition (Fig. 12a) should have a negative rotation of the same absolute magnitude, in conformity with the sum rule for rotational strengths (eqn. 22). Since the parallel and the perpendicular transition of the α-helix have a small energy separation and rotational strengths of equal magnitude and opposite sign, the two terms that they contribute to the expression for the molecular rotation (eqn. 23) give, when combined, an equation denoting an abnormal dependence of the rotation upon the fourth powei of the wavelength,[88]

$$[M']_\lambda = b_0\lambda_0^4/(\lambda^2 - \lambda_0^2)^2, \qquad (45)$$

where $[M']_\lambda$ is the contribution of the two allowed transitions of the α-helix to the molecular rotation per amide residue at the wavelength λ, and λ_0 is the average of the wavelength maxima of the absorption given by the two transitions, b_0 being a constant.

The abnormal rotatory dispersion observed[98] for poly-L-glutamic acid and other polypeptides derived from L-amino-acids in solvents favouring the α-helix conformation, give experimental values of $b_0 \approx -640°$ and $\lambda_0 \approx 2100$ Å for the constants of equation (45), compared with Moffitt's theoretical values,[88] $b_0 = -580°$ and $\lambda_0 = 2000$ Å. The polarized absorption spectra of orientated films of poly-L-alanine and poly-γ-methyl-L-glutamate place the absorptions due to the parallel and the perpendicular transitions of the α-helix at 2060 and 1910 Å, respectively,[99]

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[97] Bamford, Brown, Elliott, Hanby, and Trotter, *Proc. Roy. Soc.*, 1953, *B*, **141**, 49.
[98] Moffitt and Yang, *Proc. Nat. Acad. Sci.*, 1956, **42**, 596.
[99] Gratzer, Holzwarth, and Doty, *Proc. Nat. Acad. Sci.*, 1961, **47**, 1785.

corresponding to an energy separation, $\Delta\nu = -2700$ cm.$^{-1}$, in agreement with Moffitt's theoretical value.[88] In aqueous solution the absorption due to the parallel transition appears as a shoulder at 2050 Å upon the more intense band at 1900 Å, due to the perpendicular transition, in the spectrum[92] of the α-helix form of poly-L-glutamic acid, and the corresponding circular dichroism maxima lie[100] at 2160 and 1920 Å, respectively (Fig. 11).

From the areas of the circular dichroism bands the rotational strengths of the parallel and the perpendicular transitions given by poly-L-glutamic acid in the α-helix conformation are estimated[100] to be -41 and $+36$, respectively, in units of 10^{-40} c.g.s., whilst the rotational strength of the amide absorption due to the random-coil conformation[100] is -14 in the same units. Since the energy interval between the parallel and the perpendicular transitions of the α-helix is about one-half of the band width of the resultant absorption, the respective circular dichroism bands overlap and mutually cancel to some degree, so that the absolute magnitudes of the rotational strengths are larger than the values obtained experimentally from the solution circular dichroism measurements. The agreement between experiment and theory supports Moffitt's assumption, now established[101] by the *X*-ray diffraction study of myoglobin, that polypeptides derived from the L-amino-acids form a right-handed α-helix.

Moffitt assumed[88] further that a polypeptide in the α-helix conformation could be treated as a re-entrant system, and he employed cyclic boundary conditions in his theory. Moffitt, Fitts, and Kirkwood later showed[102] that, without these boundary conditions, there was an additional contribution to the rotational strength, directed perpendicular to the axis of the α-helix. The original terms (eqn. 42) and the additional term in the expression for the rotational strength of the α-helix appeared to be of comparable magnitude, and it was suggested[102] that the agreement between Moffitt's early theory[88] and experiment was illusory.

However, the additional term is significant only as an end-correction, and it is important only in a helical segment consisting of a few amide groups. The quasi-symmetric coupling of the $\pi\rightarrow\pi$ transitions of two amide chromophores composing a segment of the α-helix (Fig. 12c) makes two contributions to the rotational strength of the segment. Both contributions are negative in sign, and one is directed parallel, $R^{s}_{\parallel}$, and the other perpendicular, $R^{s}_{\perp}$, to the axis of the helix, namely,

$$R^{s}_{\parallel} = 2\pi\nu dD \cos t \cos v \sin^2(\pi/P), \tag{46}$$

$$\text{and } R^{s}_{\perp} = -\pi\nu ZD \cos^2 t \sin(2\pi/P)/2, \tag{47}$$

where Z is the rise per residue along the helix axis, and $2\pi/P$ is the angle between two adjacent amide residues about the helix axis (Fig. 13).

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[100] Holzwarth, Gratzer, and Doty, *J. Amer. Chem. Soc.*, 1962, **84**, 3194.

[101] Kendrew, Dickerson, Strandberg, Hart, Davies, Phillips, and Shore, *Nature*, 1960, **185**, 422.

[102] Moffitt, Fitts, and Kirkwood, *Proc. Nat. Acad. Sci.*, 1957, **43**, 723.

Similarly, the quasi-antisymmetric coupling of two amide-group excitations makes two contributions to the rotational strength of the segment (Fig. 12d). Both of the contributions have a positive sign, and both are directed perpendicular to the helix axis, namely,

$$R^{a}_{\perp} = -2\pi\nu dD \cos t \cos v \sin^2 (\pi/P), \tag{48}$$

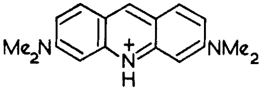
$$\text{and } R^{a'}_{\perp} = \pi\nu ZD \cos^2 t \sin (2\pi/P)/2. \tag{49}$$

The original terms of Moffitt's theory[88] are those of equations (46) and (48), and the additional terms of the Moffitt, Fitts, and Kirkwood treatment[102] are those of equations (47) and (49).

In the polypeptide α-helix there are, in general, two residues adjacent to any given amide group, disposed at angles of $\pm(2\pi/P)$ to it about the helix axis. The interaction of the $\pi \rightarrow \pi$ transition moment of the amide group with those of the adjacent residues contributes terms to the rotational strength of the α-helix according to equations (46)—(49). The contributions determined by equations (47) and (49) cancel one another, since they depend upon $\sin (2\pi/P)$, which is negative for one residue and positive for the other, whereas the contributions governed by equations (46) and (48) are additive, as they depend upon $\sin^2 (\pi/P)$.

Similar considerations apply to the coupling of the excitation moment of a given amide group with those of its two *m*th neighbours, and to interactions involving the terminal residues. Physically the sum of the contributions to the rotational strength of the α-helix determined by equation (47) or (49) vanishes when N is large, because the terms depend only upon the tangential components of the amide excitation moments. The tangential components, $\rho \cos t$ (Fig. 13), interact in the quasi-symmetric coupling mode of the α-helix (Fig. 12a) to give only a magnetic moment, and in the quasi-antisymmetric mode (Fig. 12b) to give only an electric moment, so that in neither case are the conditions (eqn. 18) for a non-zero rotational strength fulfilled.

When absorbed upon poly-L-glutamic acid in solution, cationic dyes, such as Acridine Orange (24), give anomalous rotatory dispersion in the region of the long-wavelength absorption band of the dye if the polypeptide has the α-helix conformation, but not if it has the random coil form.[103] Two Cotton effects are observed, one with a negative and the other with a positive sign, having inflection points at 4680 and 5100 Å, respectively, in the case of the dye (24). The negative effect has an amplitude of 150,000°, which does not vary with the ionic strength or with a ratio of glutamate residues to dye molecules between 10 and 10^4, whereas the positive effect is zero for small ratios and low ionic strengths and attains in media of high ionic strength a maximum molecular amplitude of



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[103] Stryer and Blout, *J. Amer. Chem. Soc.*, 1961, **83**, 1411.

300,000° at a residue-to-dye ratio of ~500. Poly-D-glutamic acid and Acridine Orange give corresponding Cotton effects with opposite signs, and analogous results are obtained with other cationic dyes which spontaneously aggregate in solution. The induced Cotton effects are ascribed[103] to helical arrays of the dye molecules, formed either by the ordered, end-to-end, absorption of the dye molecules along the length of the polypeptide α-helix, or by the tangential aggregation of the dye molecules, the sense of the helical aggregate being determined by that of the polypeptide α-helix.

Polynucleotides and nucleic acids give anomalous rotatory dispersion in the 2800 Å absorption region of the purine and pyrimidine residues.[104] When deoxyribonucleic acid is denatured, the amplitude of the Cotton effect falls and the rotation maximum moves to longer wavelengths. Vinyl polymers formed from optically active olefins, or from racemic olefins by using a dissymmetric catalyst, have a rotatory power larger than that given by the asymmetric carbon atoms alone, owing to the helical coiling of the hydrocarbon chain in a unique sense,[105] and recently, racemic vinyl polymers have been resolved.[106]

Complexes of Metal Ions.—After Cotton's[6] and Werner's work[20] the optical rotatory powers of transition-metal complexes were extensively investigated by Kuhn,[9] Jaeger,[10] and Mathieu,[11] with the aim of establishing the absolute or the relative configurations of the complexes. However, the optical methods proposed were found[107] to be at variance with the solubility methods[108,109] used to relate the chiralities of different complex ions, and the model of Kuhn and Bein[110] ascribed to the (+)-tri(ethylenediamine)cobalt(III) ion the absolute configuration enantiomeric with that (3) established[38] by *X*-ray-diffraction studies. Until the advent of the ligand-field theory, the electronic transitions responsible for the absorption of radiation and the rotatory power of metal complexes were not understood in any detail, and it was the combination of the one-electron optical rotatory power and the ligand-field theories by Moffitt[111] and subsequent workers[112-117] that provided the basis for recent spectroscopic[48] and stereochemical[43] applications.

[104] Fresco, *Tetrahedron*, 1961, **13**, 185.

[105] Pino and Lorenzi, *J. Amer. Chem. Soc.*, 1960, **82**, 4745; Bailey and Yates, *J. Org. Chem.*, 1960, **25**, 1800.

[106] Pino, Ciardelli, Lorenzi, and Natta, *J. Amer. Chem. Soc.*, 1962, **84**, 1487.

[107] Jaeger, *Proc. K. Ned. Akad. Wet.*, 1937, **40**, 108.

[108] Werner, *Ber.*, 1912, **45**, 1229.

[109] Delepine, *Bull. Soc. chim. France*, 1934, **1**, 1256.

[110] Kuhn and Bein, *Z. phys. Chem.*, 1934, *B*, **24**, 335.

[111] Moffitt, *J. Chem. Phys.*, 1956, **25**, 1189.

[112] Sugano, *J. Chem. Phys.*, 1960, **33**, 1883.

[113] Sugano, Internat. Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962.

[114] Hamer, *Mol. Phys.*, 1962, **5**, 339.

[115] Piper, *J. Chem. Phys.*, 1962, **36**, 2224.

[116] Piper and Karipides, *Mol. Phys.*, 1962, **5**, 475.

[117] Liehr, "Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961.

The classical measurements of the rotatory dispersion and the circular dichroism of transition-metal complexes, together with subsequent determinations, show (Fig. 15, Table 5) that of the various ligand-field absorptions given by a particular metal complex the band due to the spin-allowed $d \rightarrow d$ electronic transition of lowest energy has the largest rotatory power. The ligand-field theory indicates that this transition is generally magnetic dipole-allowed, and that it is the only $d \rightarrow d$ transition allowed in magnetic dipole radiation fields for d^3 and strong-field d^6 complexes, a class to which the majority of the available dissymmetric complexes belong. Rotations in the octahedral group O_h belong to the triply-degenerate representation T_{1g}, and electronic transitions with T_{1g} symmetry are magnetic dipole-allowed in octahedral complexes. Dihedral metal complexes belong to the group, D_3, in which T_{1g} goes over into the representations A_2 and E, the latter being doubly degenerate. In terms of the symmetries of the electronic states in dihedral complexes, the selection rules for allowed electronic transitions are

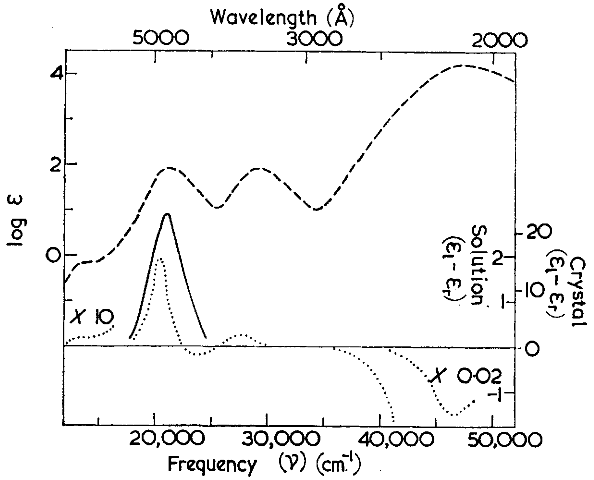

FIG. 15. *The circular dichroism (........) and the absorption spectrum (-----) of the* (+)-*tri*(*ethylenediamine*)*cobalt*(III) *ion in aqueous solution, and the circular dichroism of the crystal,* $2[(+)\text{-Co en}_3\text{Cl}_3]\ \text{NaCl},6H_2O$ (——), *for radiation directed along the optic axis.*

$$\begin{aligned} A_1 &\longleftrightarrow A_2\ (\parallel), \\ A_1, A_2 &\longleftrightarrow E\ (\perp), \\ E &\longleftrightarrow E\ (\parallel, \perp), \end{aligned} \qquad (50)$$

the moments being polarized parallel (||) or perpendicular (⊥) to the principal axis (C_3) of the chelated complex (Fig. 16).

TABLE 5. *Electronic absorption and circular dichroism spectra of transition-metal complexes.*

Complex	Absorption		Circular Dichroism		Transition	Ref.
	$\lambda_{max.}$ (Å)	ϵ	$\lambda_{max.}$	$(\epsilon_l - \epsilon_r)$		
(+)-Tri(ethylenediamine)-cobalt(III)	7300	0·35	7300	+0·008	$^1A_1 \rightarrow {}^3A_2, {}^3E$	*p*
	4690	84	4930	+1·89	$^1A_1 \rightarrow {}^1E_a$	
			4280	−0·166	$^1A_1 \rightarrow {}^1A_2$	
	3400	74	3610	+0·250	$^1A_1 \rightarrow {}^1E_b$	
	2080	15,000	2150	−60	Charge transfer	
Hexamminecobalt(III)	4760	60			$^1A_{1g} \rightarrow {}^1T_{1g}$	*p*
	3420	44			$^1A_{1g} \rightarrow {}^1T_{2g}$	
(−)-Trioxalatocobalt(III)	5990	143	6170	+1·80	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	122
	4180	210	4000	−0·20	$^1A_1 \rightarrow {}^1E_b$	
	2750	15,000			Charge transfer	
Tri-(+)-hydroxymethylene-camphor)cobalt(III)	6070	130	7100	−0·50	$^1A_1 \rightarrow {}^1A_2$	*g*
			6030	+6·20	$^1A_1 \rightarrow {}^1E_a$	
	4250	460	4520	−8·0	$^1A_1 \rightarrow {}^1E_b$	
	3480	710	3600	−69	Charge transfer	
(+)-Tri(ethylenediamine) chromium(III)	4560	76	4600	+1·7	$^4A_2 \rightarrow {}^4A_1, {}^4E_a$	*p*
	3480	66	3600	−0·3	$^4A_2 \rightarrow {}^4E_b$	
(+)-Trioxalato-chromium(III)	5700	80	6300	−0·6	$^4A_2 \rightarrow {}^4A_1$	*p*
			5550	+2·9	$^4A_2 \rightarrow {}^4E_a$	
	4200	100	4150	−1·0	$^4A_2 \rightarrow {}^4E_b$	
Tri-(+)-hydroxy-methylcamphor-chromium(III)	5590	60	6300	−0·78	$^4A_2 \rightarrow {}^4A_1$	*g*
			5550	+4·10	$^4A_2 \rightarrow {}^4E_a$	
	4620	180	4780	+0·46	$^4A_2 \rightarrow {}^4E_b$	
	4100	440	<4200	<−1·3	Charge transfer	
(−)-Tri(ethylenediamine) rhodium(III)	3050	200	3100	+1·4	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	*p*
(−)-Trioxalatorhodium (III)	4000	300	4100	+3·0	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	*p*
(−)-Tri(ethylenediamine)-iridium(III)	3100	500	3150	+0·4	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	*p*
(+)-Trioxalatoiridium(III)	4400	100	4600	+1·0	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	*q*
Manganese(III) (+)-tartrate	4560	352	5350	+0·82	$^5E_a \rightarrow {}^5E_b, {}^5A_1$	*r*
			4250	−0·93		
					Components of:	
Cobalt(II) (+)-tartrate	11,200	4·1	12,250	+0·35	$^4T_{1g} \rightarrow {}^4T_{2g}$(F)	*r*
	5700	12·7	5700	−0·32	$^4T_{1g} \rightarrow {}^4A_{2g}$(F),$^4T_{1g}$(P)	
					Components of:	
Nickel(II) (+)-tartrate	11,200	6·3	12,000	+0·59	$^3A_{2g} \rightarrow {}^3T_{2g}$(F)	*r*
	6950	8·2	6850	−0·10	$^3A_{2g} \rightarrow {}^3T_{1g}$(F)	
	3950	20	4000	−0·12	$^3A_{2g} \rightarrow {}^3T_{1g}$(P)	
					Components of:	
Copper(II) (+)-tartrate	6600	30	7750	−0·06	$^2E_g \rightarrow {}^2T_{2g}$	*r*
			6200	+0·26		

References: (*g*) See Table 2. (*p*) McCaffery and Mason, *Mol. Phys.*, in the press. (*q*) Mathieu, *J. Chim. phys.*, 1936, **33**, 78. (*r*) McCaffery and Mason, unpublished results.

Most $d \rightarrow d$ transitions are both electric and magnetic dipole-allowed by these selection rules, but the absorption spectra of dihedral co-ordination compounds do not differ markedly from those of the corresponding octahedral complexes (Table 5), indicating that the more rigorous selection rules for O_h are strong, and that the rules for D_3 are weak. Thus an electronic transition with a large magnetic moment in a dihedral complex has a T_{1g} parentage in the corresponding octahedral complex.

The total magnetic moment of all the electronic transitions from the ground state of a given metal ion[118] is $\sqrt{L(L+1)}\beta_M$, where L is the electronic orbital angular momentum of the ground state. If only one transition is magnetic dipole-allowed the entire moment is concentrated in that transition, so that the long-wavelength absorption bands of octahedral chromium(III) and cobalt(III) should be due to transitions with magnetic moments of $\sqrt{12}\beta_M$ and $\sqrt{24}\beta_M$, respectively.[111] These moments are isotropic, and in the corresponding dihedral ions the magnetic moments of the derived A_2 and E transitions are, respectively, $2\beta_M$ and $2\sqrt{2}\beta_M$ for chromium(III) and $2\sqrt{2}\beta_M$ and $4\beta_M$ for cobalt(III).

The $d \rightarrow d$ transitions with A_2 and E symmetry in a dihedral metal complex attain a rotational strength by acquiring a small part of the electric moment of a higher-energy transition with the same symmetry. The rotational strengths of an A_2 and an E transition with a common T_{1g} octahedral parentage are necessarily opposed in sign,[112,114] since the chiralities of a given dihedral metal complex parallel and perpendicular to the principal axis are complementary, *e.g.*, the helicity of a compound (3) is left-handed along the three-fold axis but right-handed along a two-fold axis.

The energy interval between an A_2 and an E transition with a common parentage is small,[119,120] and the dipole strengths of the two transitions give a single absorption band in the solution spectrum of the dihedral ion, whilst the two rotational strengths largely cancel one another and give, in general, two residual wing circular dichroism absorptions with opposed signs (Table 5, Fig. 15). However, if circularly polarized light is propagated along the three-fold rotation axis of a dihedral metal complex, the radiation field can give rise only to electronic transitions with E symmetry, and the rotational strengths of such transitions may then be measured directly.

In the hexagonal double salt, $2[(+)\text{-Co en}_3\text{Cl}_3]\text{NaCl},6\text{H}_2\text{O}$, the C_3 axis of each complex ion is parallel to the optical axis of the crystal,[38] and the circular dichroism spectrum, measured with the radiation propagated along the optic axis of the crystal,[121] indicates (Fig. 15) that in solution the rotational strengths of the A_2 and the associated E transition cancel to within 5%. The crystal circular dichroism spectrum of the (+)-tri-

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[118] Griffith, "The Theory of Transition Metal Ions," Cambridge Univ. Press, 1961.
[119] Piper and Carlin, *J. Chem. Phys.*, 1961, **35**, 1809.
[120] Yamada and Tsuchida, *Bull. Chem. Soc. Japan*, 1960, **33**, 98.
[121] McCaffery and Mason, *Mol. Phys.*, in the press.

(ethylenediamine)cobalt(III) ion gives the spin-allowed E transition of lowest energy (^1E_a) a rotational strength of 79×10^{-40} c.g.s., a somewhat larger value, 108×10^{-40} c.g.s., being obtained from the corresponding optical rotatory dispersion curve.[121]

The crystal spectrum of the ion[121] gives the dipole strength of the ^1E_a transition at 4690 Å as 1500×10^{-40} c.g.s., and the corresponding absorption at 4760 Å of the analogous octahedral complex, the hexamminecobalt(III) ion, has[121] a dipole strength of 880×10^{-40} c.g.s. The difference between these dipole strengths represents the square of the additional electric moment acquired by the ^1E_a transition due to the reduction in symmetry from octahedral to dihedral. The additional electric moment and the rotational strength give, with a zero angle, θ (eqn. 18), a magnetic moment of $3{\cdot}4\beta_M$ from the circular dichroism spectrum and of $4{\cdot}3\beta_M$ from the corresponding rotatory dispersion curve for the ^1E_a transition of the dihedral cobalt(III) ion, in satisfactory agreement with the theoretical value ($4{\cdot}0\beta_M$).

The shorter-wavelength ligand-field absorption band of octahedral cobalt(III) is due to an electronic transition with $^1T_{2g}$ symmetry, which breaks down into components with $^1A_1$ and ^1E symmetry in the corresponding dihedral complex. The latter transition may be designated ^1E_b in order to distinguish it from the lower-energy ^1E_a transition. The transition $^1A_1 \rightarrow {}^1A_1$ is forbidden in the dihedral complex (eqns. 50), and the circular dichroism band at 3610 Å in the spectrum of the (+)-tri(ethylenediamine)cobalt(III) ion (Fig. 15, Table 5) may be ascribed to the ^1E_b component. The difference between the dipole strengths of the 3400 Å absorption given by the triethylenediamine and the hexammine complex of cobalt(III) measures the square of the additional electric moment acquired by the ^1E_b transition owing to the lower symmetry of the dihedral complex. The additional electric moment, together with the observed[121] rotational strength of the 3610 Å circular dichroism absorption, gives (eqn. 18) a magnetic moment of $0{\cdot}023\beta_M$ for the ^1E_b transition.

The $^1A_1 \rightarrow {}^1E_b$ transition of dihedral cobalt(III) complexes attains a rotational strength by borrowing a small part of the magnetic moment of the transition to the ^1E_a state. Having the same symmetries, and an energy separation of only 8000 cm.$^{-1}$, the two ^1E states are mixed. The degree of mixing is represented by the ratio of the estimated magnetic moments, that is, the first-order ^1E_b state contains about 0·5% of the zero-order ^1E_a state. Similarly the spin-forbidden transition responsible for the weak absorption at 7300 Å in the spectrum of the (+)-tri(ethylenediamine)cobalt(III) ion (Fig. 15, Table 5) acquires a rotational and a dipole strength by the mixing of the triplet, $^3A_2$ and ^3E, upper states with the corresponding singlet, $^1A_2$ and ^1E_a, states of the same orbital symmetry.

Most quantum-mechanical theories of the rotatory power of transition-metal complexes[111–117] are based on the ionic crystal-field model, wherein it is assumed that six point charges at the vertices of an octahedron around a central metal ion are displaced parallel to a three-fold rotation axis, giving the structure dihedral symmetry. The resultant trigonal field mixes the metal *d*-orbitals with metal atomic orbitals of odd symmetry, notably, *p*- or *f*-orbitals, and the rotational strength of the dihedral complex is due to the addition of a small contribution from the electric dipole-allowed $d \rightarrow p$ or $d \rightarrow f$ transition to the magnetic dipole-allowed $d \rightarrow d$ transition. However, the ionic model gives, for the $^1A_2$ and ^1E_a transitions of the (+)-tri(ethylenediamine)cobalt(III) ion (3), rotational strengths which are too small, are incorrect in sign, and lie in the wrong energy order.

The crystal-field model, which involves mixing metal *d*- and *p*-orbitals, was introduced by Moffitt,[111] who attributed rotational strengths of the same sign to the $^1A_2$ and ^1E_a transitions of dihedral cobalt(III), through an error of sign in the values of the electronic angular momentum changes involved in $d \rightarrow d$ transitions.[112-116] Correcting the error, a later calculation[114] assigned rotational strengths of opposed signs to the two transitions, and gave an absolute value of 16×10^{-40} c.g.s. for the rotational strength of each excitation. This estimate is somewhat small, and it requires[114] an energy interval between the $^1A_2$ and the ^1E_a state of the (+)-tri(ethylenediamine)cobalt(III) ion of some 500 cm.$^{-1}$, which is an order of magnitude larger than the splitting between the corresponding absorptions observed[120,122] in the polarized spectra of crystals containing the ion. When the experimental energy interval between the $^1A_2$ and the ^1E_a transition is used, a rotational strength of no more than $\sim 2 \times 10^{-40}$ c.g.s. for each transition can be sustained for the case of *d–p* mixing, and the rotational strengths for *d–f* mixing[116] are an order of magnitude smaller.

The ionic model predicts further[115,116] that in the (+)-tri(ethylenediamine)cobalt(III) ion, which has[38] the absolute configuration (3), the transitions to the $^1A_2$ and the ^1E_a states should have positive and negative rotational strength, respectively, with the latter state lying at the higher energy. However, the experimental circular dichroism spectra of the ion (Fig. 15) establish unequivocally[121] that the transition to the ^1E_a state has the lower energy and a positive rotational strength.

A theoretical limitation to the ionic model, depending as it does on the mixing of the *d*-orbitals with metal atomic orbitals of odd symmetry, is the high energy ($\sim 10^5$ cm.$^{-1}$) of the $d \rightarrow p$ and $d \rightarrow f$ transitions. Electric dipole transitions of lower energy, notably, those involving ligand molecular orbitals of odd symmetry, should combine more intimately with the metal-ion $d \rightarrow d$ transitions, but such a mixing is envisaged only in the molecular-orbital ligand-field scheme, and not in the crystal-field model. The electric dipole transition of lowest energy in a metal co-ordination compound gives rise to the charge-transfer band, observed at 2000 Å for the amine complexes and at 2500 Å for the carboxylic acid complexes (Table 5), and on energy grounds the charge-transfer absorption provides the most probable source of the additional dipole strength and the rotatory

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[122] Piper, unpublished results.

power acquired by the visible absorption bands of metal complexes on the reduction of symmetry from octahedral to dihedral.

In classical terms, such a source was postulated in the coupled anisotropic oscillator model of Kuhn and Bein.[110] These authors assumed that the charge-transfer absorption was due to ligand transitions with electric moments directed along the three edges of the octahedron spanned by chelate rings in the dihedral complex (Fig. 16). The three ligand moments coupled one with the other, and with an electronic oscillation of the metal ion, to give two perturbed metal-ion transitions with nearly the same energy, one with A_2 and the other with E symmetry. In general, the A_2 and the E transition of the metal ion had rotatory powers of opposite sign, but for a small range of values of the coupling coefficients the rotatory powers of the two transitions were shown to have the same sign, and the complex studied, the (—)-trioxalatocobalt(III) ion, was thought to have coupling coefficients within this range, as the complex gave a single circular dichroism absorption under the 6000 Å band (Table 5). From the calculated sign of the rotatory power, Kuhn indicated[123] that dihedral metal complexes with the absolute configuration (3) should be lævorotatory in the red wavelength region, but it is now known[38] that the tri(ethylenediamine)cobalt(III) enantiomer with the chirality (3) is dextrorotatory in that region.

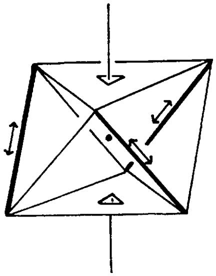

FIG. 16. *The classical model of Kuhn and Bein.*[110] *Thickened lines denote octahedral edges spanned by chelate rings, and the arrows give the assumed directions of the ligand transition moments.*

Contrary to the assumption of Kuhn and Bein,[110] the ligand charge-transfer band observed in the spectrum of the (+)tri(ethylenediamine)-cobalt(III) ion at 2080 Å (Table 5, Fig. 15) appears to be due to electronic transitions polarized perpendicular to the planes of the chelate rings. The long-wavelength part of the charge-transfer absorption is due mainly to a

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[123] Kuhn, *Naturwiss.*, 1938, **26**, 289.

transition with *E* symmetry, since plane-polarized radiation propagated perpendicular to the optic axis of the various tri(ethylenediamine)cobalt(III) halide crystals studied by Yamada and Tsuchida[120] is more strongly absorbed in the 3000—2500 Å wavelength region if the electric vector of the radiation is oriented perpendicular, as opposed to parallel, to the optic axis. In the same wavelength region the circular dichroism given by the (+)-tri(ethylenediamine)cobalt(III) ion is negative in sign (Fig. 15), indicating that the charge-transfer transition with *E* symmetry has a negative rotational strength. This assignment, together with the established[38] absolute configuration (3) of the ion, requires, according to the coupled oscillator theory,[88] that the individual charge-transfer excitations at each of the six ligand positions have moments directed perpendicular to the planes of the chelate rings. Such excitations couple to give two allowed transitions, one with A_2 and the other with *E* symmetry, the former having a positive and the latter a negative rotational strength.[121]

The establishment of the sign of the rotational strength is derived from a particular electronic transition in a metal complex with a known absolute configuration provides the basis of an optical method[43] for relating the chiralities of metal complexes generally. The classical optical methods for relating the absolute configurations of metal co-ordination compounds were based upon the sign of the rotation given by the complexes at the sodium D-line,[124] or, more significantly, upon the sign of the long-wavelength Cotton effect, measured either by the circular dichroism or by the anomalous optical rotatory dispersion.[107] In dihedral d^3 and d^6 complexes the long-wavelength Cotton effect may be due to either the A_2 or the E_a transition, depending upon the relative energies of the two excitations. The two transitions have rotational strengths with opposed signs, and metal complexes with the same absolute configuration may give long-wavelength Cotton effects with different signs, as is shown by the discrepancy between the classical optical and solubility methods for relating the chiralities of metal complexes.[107]

The criterion[43] that dihedral d^3 and d^6 metal complexes have the absolute configuration (3) if the E_a transition has a positive rotational strength is, however, in accord with the classical solubility assignments of chirality to dihedral complexes.[108,109] The sign of the rotational strength of the E_a transition is given directly by circular-dichroism and rotatory-dispersion measurements made with the active complex ion oriented in a crystal,[125-127] and the sign may be obtained indirectly[128] from the solution circular dichroism of the active complex and either the relative energies of the A_2 and the E_a transitions, or the intensity ratio of the two absorptions, determined from the polarized crystal absorption spectrum of the racemic

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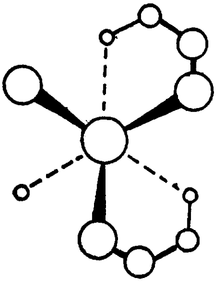
[124] Werner, *Bull. Soc. chim. France*, 1912, **11**, 1.
[125] Mathieu, *Compt. rend.*, 1953, **236**, 2395.
[126] Jaeger, Ter Berg, and Terpstra, *Proc. K. Ned. Akad. Wet.*, 1937, **40**, 574.
[127] Longchambon, *Compt. rend.*, 1924, **178**, 1828.
[128] McCaffery and Mason, *Trans. Faraday Soc.*, 1963, **59**, 1.

complex,[119,120,129] In general, the E_a transition has the larger rotational strength, and it gives rise to the more intense of the two circular-dichroism absorptions appearing under the long-wavelength absorption band of a dihedral complex ion in solution (Fig. 15). In the cases where a single circular-dichroism absorption is observed under the long-wavelength absorption band, owing to the small energy splitting of the A_2 and the E_a transition, notably, (—)-trioxalatocobalt(III) and (+)-tri(ethylenediamine)-chromium(III) (Table 5), the circular dichroism takes its sign from that of the rotational strength of the E_a transition.

The complexes of chromium(III) and cobalt(III) which have the absolute configuration (3), giving a circular dichroism absorption due to the E_a transition with a positive sign (Table 5), are[43] the ethylenediamine complexes with the less soluble chloro-(+)tartrate salt, the oxalate complexes with the less soluble (—)-strychnine salt, and the more stable of the neutral enantiomeric complexes formed with the β-dicarbonyl ligand, (+)-hydroxymethylenecamphor. Werner's method[108] of relating absolute configuration through the solubilities of the salts formed by a given optically active gegen-ion with different complexes of the same charge type, and Delepine's method[109] of active racemates, cannot link the chiralities of the cationic, neutral, and anionic complexes, whereas an optical method affords such a connection.

The rotatory powers of metal complexes with a symmetry lower than D_3 have been widely investigated,[130-139] but, as yet, the electronic transitions responsible for the rotatory power have not been characterised experimentally in any detail. The dissymmetric co-ordination compounds most closely related to the dihedral complexes are the *cis*-complexes with



(25)

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[129] Piper and Carlin, *J. Chem. Phys.*, 1962, **36**, 3330.
[130] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.
[131] Mathieu, *Ann. Phys.*, 1944, **19**, 335.
[132] Mathieu, *Bull. Soc. chim. France*, 1938, **5**, 105, 773.
[133] Pfeiffer, Christeleit, Hesse, Pfitzner, and Thielert, *J. prakt. Chem.*, 1938, **150**, 261.
[134] Pfeiffer, *Ber.*, 1944, **77**, *A*, 59.
[135] Pfeiffer and Saure, *Ber.*, 1941, **74**, 935.
[136] Jaeger and Blumendal, *Z. anorg. Chem.*, 1928, **175**, 161.
[137] Morgan and Smith, *J.*, 1925, **127**, 913, 2030.
[138] Dwyer and Lions, *J. Amer. Chem. Soc.*, 1950, **72**, 1545.
[139] Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 2925.

two bifunctional chelate bridges and two monodentate ligands (25). The circular dichroism, rotatory dispersion, and absorption spectra of the complexes, *cis*-M en$_2$AA′, where M = tervalent chromium, cobalt, or iridium, en = ethylenediamine, and A,A′ = carbonate, oxalate, ammonia, water, chloride, bromide, thiocyanate, or nitro, were measured by Mathieu,[130] who observed that such complexes gave, in general, two circular dichroism absorptions with opposed signs under the long-wavelength absorption band.

In the *cis*-complexes with C_2 symmetry (25) the triply degenerate T_{1g} transition of the corresponding octahedral complex breaks down into one component with A symmetry and two components with B symmetry, the former being directed parallel and the latter perpendicular to the two-fold rotation axis. The transition with A symmetry is derived from the component of the doubly degenerate E_a transition of the corresponding dihedral complex (3) directed along the C_2 axis which becomes the principal axis of the *cis*-complex (25), whilst the other E_a component and the A_2 component of the dihedral complex (3) become transitions with B symmetry in the *cis*-complex (25). The model ascribing the rotatory power of the visible absorption bands of metal complexes to the mixing of the metal-ion transitions with ligand transitions directed perpendicular to the planes of the chelate rings[121] indicates that *cis*-complexes with an absolute configuration (25) related to that of the dihedral complex (3) should give a transition of A symmetry with a positive rotational strength.

The *trans*-complexes isomeric with the *cis*-complex (25) exhibit circular dichroism and anomalous rotatory dispersion in the region of the long-wavelength absorption bands if the two bidentate bridge ligands are themselves optically active[131,136] The planar co-ordination compounds derived from such *trans*-complexes by the removal of the two axial monodentate ligands display a similar rotatory power in the visible-wavelength region.[133] Complexes containing tridentate,[135] tetradentate,[137] and hexadentate[138,139] ligands have been resolved, and they give anomalous rotatory dispersion in the wavelength region of the metal-ion absorption bands.

The optical rotatory power of complexes containing lanthanide or actinide metal ions has not been extensively studied as yet. Anomalous rotatory dispersion in the visible-wavelength region has been reported for uranyl[140] and neodymium tartrate,[141] and for the uranyl derivative of hydroxymethylenecamphor.[142]

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[140] Bruhat, *Ann. Phys.*, 1915, **3**, 417.
[141] Gray, *Phys. Rev.*, 1916, **7**, 472.
[142] Lifschitz, *Z. phys. Chem.*, 1923, **105**, 27.