304. *The Magnetic Dipole Character and the Rotatory Power of $n \rightarrow \pi^*$-Transitions.   Part II.†   The Circular Dichroism of a 17-Oxo- and a 17-Thioxo-steroid.*

By R. E. BALLARD and S. F. MASON.

The circular dichroism and the absorption spectra of epiandrosterone and of the corresponding thione have been measured in ethanol solution. The magnetic moment of the transition responsible for the 5000 Å thiocarbonyl absorption is found to have the value 0·62 Bohr magneton, when the previously determined value (1·0 β_M) is used for the 3000 Å carbonyl absorption. The contributions of the groups conferring dissymmetry on epiandrosterone to the rotatory power of the 3000 Å absorption are assessed. The contribution of the 18-methyl group is shown to be much smaller than that of the atoms of rings A, B, and C. The effect is explained by the relative electron-donating capacities of the groups as measured by the ionisation potentials, which are larger for primary than for secondary, tertiary, or quaternary alkyl groups.

IN principle, electronic transitions of the $n_p \rightarrow \pi^*$ type are allowed in magnetic dipole radiation fields, as the excitation involves a rotatory displacement of the promoted electron. However, a magnetic dipole transition moment of one Bohr magneton (β_M) gives an oscillator strength only of the order of 10^{-6}, whereas the $n \rightarrow \pi^*$ transitions of polyatomic molecules are found to have oscillator strengths of the order of 10^{-4} or greater. Most of the absorption intensity is acquired by the mixing of the $n \rightarrow \pi^*$ transition with an electric dipole transition, the mixing arising from structural asymmetries, or from the non-totally symmetric vibrations of molecules with high symmetry.[1] Thus $n \rightarrow \pi^*$ transitions cannot be characterised as magnetic-dipole-allowed by methods which depend upon the detection of a magnetic dipole strength.[2,3]

The rotatory power of an optically active molecule is derived from electronic transitions which have both an electric and a magnetic moment, requiring the concerted interaction of the electric and the magnetic radiation field with the promoted electron.[4] The rotational strength of such a transition may be readily determined in cases where the contribution of the magnetic moment to the total dipole strength is very small, and the measurement of the absorption and the circular-dichroism spectrum of a dissymmetric molecule provides a unique method for the identification of a magnetic-dipole-allowed transition with a borrowed electric moment dominating the absorption.

The rotational strength, R_{ba}, of an electronic transition between the states a and b of a dissymmetric molecule is [4] the scalar product of the electric dipole, ρ, and the magnetic dipole, μ, transition moments:

$$R_{ba} = \rho\mu \cos \theta, \tag{1}$$

where θ is the angle between the directions of the two moments. Experimentally the rotational strength of the transition may be obtained [5] from the area of the corresponding circular dichroism band:

$$R_{ba} = (3hc.\ 10^3 \log_e 10/32\pi^3 N)\int[(\varepsilon_1 - \varepsilon_r)/\nu]d\nu$$
$$= 22{\cdot}9 \times 10^{-40}\int[(\varepsilon_1 - \varepsilon_r)/\nu]d\nu \tag{2}$$

† Part I. *Mol. Phys.*, 1962. **5**, 343

[1] Mason, *Quart. Rev.*, 1961, **15**, 287.
[2] Sayre, Sancier, and Freed, *J. Chem. Phys.*, 1955, **23**, 2060.
[3] Freed and Weissman, *Phys. Rev.*, 1941, **60**, 440.
[4] Condon, *Rev. Mod. Phys.*, 1937, **9**, 432.
[5] Moffitt and Moscowitz, *J. Chem. Phys.*, 1959, **30**, 648.

where ε_1 and ε_r refer, respectively, to the decadic molar extinction coefficients for left- and right-handed circularly polarised light at the frequency, ν, the rotational strength being expressed in c.g.s. units.

The dipole strength D_{ba}, of an electronic transition between the states a and b of a molecule represents [6] the sum of the squares of the electric dipole, the magnetic dipole, and the multipole transition moments. Since the magnetic dipole and any multipole moment of an $n \rightarrow \pi^*$ transition in a polyatomic molecule are very small compared with the electric moment, the dipole strength is given in good approximation by:

$$D_{ba} = \rho^2. \tag{3}$$

Experimentally the dipole strength of an electronic transition may be derived, in c.g.s. units, from the area of the corresponding absorption band [6]

$$D_{ba} = (3hc.10^3 \log_e 10/8\pi^3 N) \int (\varepsilon/\nu) \mathrm{d}\nu$$
$$= 91 \cdot 8 \times 10^{-40} \int (\varepsilon/\nu) \mathrm{d}\nu \tag{4}$$

The experimental rotational and dipole strengths of a transition then give the magnetic moment, μ, through the relation

$$\mu = R_{ba}/(\cos \theta \sqrt{D_{ba}}). \tag{5}$$

From the circular dichroism and the absorption spectrum of 3β-hydroxy-5α-androstan-16-one it has been shown,[7] by using the above relations, that the magnetic moment of the
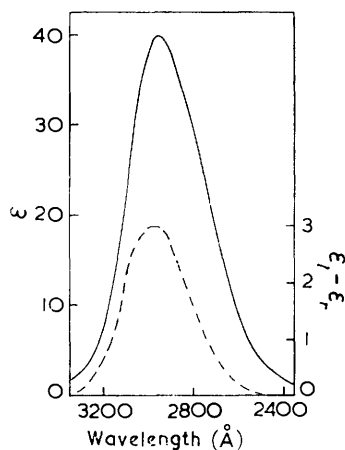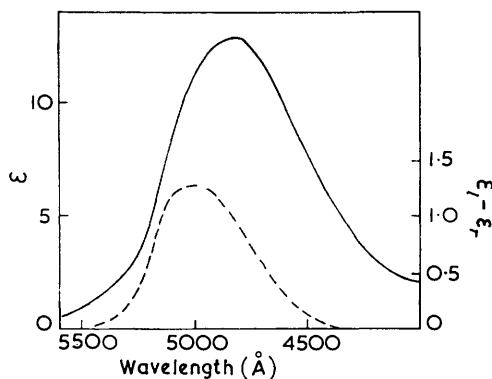

FIG. 1.

FIG. 2.

The circular dichroism (– – –) and the absorption spectrum (———) of (FIG. 1) 3β-hydr-oxy-5α-androstan-17-one and (FIG. 2) 3β-hydroxy-5α-androstane-17-thione, in ethanol.

$n \rightarrow \pi^*$ transition giving rise to the 3000 Å absorption of the carbonyl group has the experimental value of $1 \cdot 0 \ \beta_{\mathrm{M}}$, in good agreement with the theoretical value ($1 \cdot 1 \ \beta_{\mathrm{M}}$) calculated [7] from the self-consistent field orbitals of formaldehyde.[8] In the present work the magnetic moment of the $n \rightarrow \pi^*$ transition responsible for the 5000 Å absorption of the thiocarbonyl group is estimated by a different, but more approximate, method.

[6] Mulliken, *J. Chem. Phys.*, 1939, **7**, 14.
[7] Mason, *Mol. Phys.*, 1962, **5**, 343.
[8] Goodfriend, Birss, and Duncan, *Rev. Mod. Phys.*, 1960, **32**, 307; Foster and Boys, *ibid.*, p. 303.

The analysis of the circular dichroism of the 3000 Å carbonyl absorption required [7] a dissymmetric ketone with a structure approximating to C_2 symmetry in the immediate neighbourhood of the carbonyl group, such as a 16-oxo-steroid with a *trans*-c/D ring junction, and the corresponding unsubstituted monocyclic ketone, namely, cyclopentanone. The dipole strength of the 3000 Å absorption given by the 16-oxo-steroid was divided into two parts, one, due to the cyclopentanone ring, directed perpendicular to the carbonyl-bond axis, and the other, due to the substituents conferring dissymmetry upon the molecule, directed along the carbonyl bond axis owing to the approximate C_2 symmetry. Thus, a direct knowledge of the angle θ (eqns. 1 and 5) was not required.

Although 17-thioxo-steroids have been prepared,[9] the attempted synthesis of an analogous 16-thione failed,[9] and the monocyclic thioketones are too unstable to afford reliable spectroscopic data.[10] The analysis of the circular dichroism of a 17-thioxo-steroid depends upon a knowledge of the angle, θ (eqn. 5), which may be evaluated if it is assumed that the same angle, θ, obtains in the analogous transitions of a ketone and the corresponding thioketone.

The circular dichroism and the absorption spectra of 3β-hydroxy-5α-androstan-17-one (I) and of the corresponding thione (II) have been measured (Figs. 1 and 2), in the wavelength region of the $n \rightarrow \pi^*$ absorption of the unsaturated group. From the observed band areas the rotational and dipole strengths of the 3000 Å absorption given by the ketone (I) are found (eqns. 2 and 4) to be 8·2 and 520, respectively, in units of 10^{-40} c.g.s. The known [7] magnetic moment (1·0 β_M) of the carbonyl $n \rightarrow \pi^*$ transition then gives (eqn. 5) the value of the required angle as θ = 67° for this transition in the case of the ketone (I).
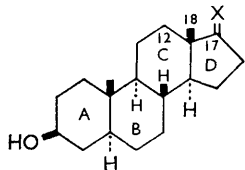
(I : X = O)   (II : X = S)

The rotational and dipole strengths of the 5000 Å absorption of the thioketone (II), obtained from the observed band areas by means of equations (2) and (4), are 3·0 and 180, respectively, in units of 10^{-40} c.g.s. These strengths give (eqn. 5) a value of 0·62 β_M for the magnetic moment of the thiocarbonyl $n \rightarrow \pi^*$ transition, on the assumption that the angle between the directions of the electric moment and the magnetic moment in the $n \rightarrow \pi^*$ transition is the same for the thioketone (II) as for the ketone (I).

The magnitude of the value obtained for the magnetic moment establishes that the 5000 Å thiocarbonyl absorption is due to a transition allowed in magnetic dipole radation fields, involving a rotatory displacement of the promoted electron. Hitherto, the 5000 Å absorption of thioketones has been ascribed to the promotion of a sulphur lone-pair electron to the antibonding π-orbital of the thiocarbonyl group largely on theoretical grounds,[11] but the present result affords experimental evidence for the assignment.

The magnetic moment of the carbonyl $n \rightarrow \pi^*$ transition is directed along the carbonyl-bond axis, and the gross electric moment of the transition, directed at an angle of 67° to that axis in the case of the ketone (I), is the vector sum of a number of contributions. In cyclopentanone the electric moment of the $n \rightarrow \pi^*$ transition is perpendicular to the carbonyl-bond axis, the molecule being optically inactive, and this moment should survive largely unchanged in any substituted cyclopentanone, although an additional electric moment is contributed by the substituents. Since the $n \rightarrow \pi^*$ transition of cyclopentanone has a dipole strength [7] of 258×10^{-40} c.g.s., approximately one-half of the dipole strength of the 3000 Å absorption given by the 17-oxo-steroid (I) is due to the substituents of ring D, namely, the atoms of rings A, B, and C, and the 18-methyl group.

The nodal planes of the oxygen $2p$ lone-pair orbital and of the carbonyl antibonding π-orbital divide the molecular environment of the carbonyl group into eight spatial

[9] Djerassi and Herbst, *J. Org. Chem.*, 1961, **26**, 4675.
[10] Janssen, *Rec. Trav. chim.*, 1960, **79**, 454, 464.
[11] McMurry, *J. Chem. Phys.*, 1941, **9**, 231, 241.

regions,[12] the intersection of the planes providing an origin approximately at the centre of the carbon–oxygen bond (III). The vector joining the 18-methyl group of the 17-oxo-steroid (I) to the origin (III) makes an angle of $\sim 30°$ with the carbonyl bond, and, according to the octant rule,[12] this group confers upon the $n \rightarrow \pi^*$ transition of ketone (I) 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 (III) are orientated at an average angle of $\sim 45°$ 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 ketone (I) 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,[12] account for the gross spectroscopic angle, $\theta = 67°$, given by the circular dichroism and the absorption spectrum (Fig. 1), if the total dipole strength of the 3000 Å absorption of the 17-oxo-steroid (I) 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.
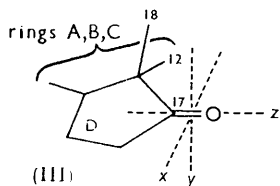
The values of the individual contributions are not greatly altered by changes in the estimated angles consistent with either of the envelope conformations or the half-chair model for ring D in 17-oxo-steroids.[13] However, the precise values of the contributions are not important, although the relative 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 as the distance between the interacting groups is increased.

This feature is explained by the charge-transfer character[7] of the electric dipole transition which mixes with the carbonyl $n \rightarrow \pi^*$ transition and confers a rotational strength and added dipole strength upon the 3000 Å absorption of dissymmetric ketones. Alkanes act as electron-donors, giving charge-transfer absorption bands with iodine[14] at 2300 Å, and the carbonyl group is an electron-acceptor, $\beta\gamma$-unsaturated ketones showing charge transfer absorption[15] near 2000 Å. The charge-transfer transition of an electron from an alkyl group to the carbonyl group in a saturated ketone gives rise to absorption in the vacuum-ultraviolet, and the degree to which such an excitation mixes with the carbonyl $n \rightarrow \pi^*$ transition depends upon the ionisation potential of the alkyl group.

In general, the ionisation potentials of alkanes lie in the order, primary $>$ secondary $>$ tertiary $>$ quaternary, relevant values being[16] 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 π^*-orbital of the ketone (I) occurs at a higher energy than is associated with the corresponding transitions from the secondary, tertiary, and quaternary alkyl groups of rings A, B, and C. In consequence, 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 ketone (I) in spite of the proximity of the 18-methyl group to the carbonyl bond.

Analogous considerations account for the small dipole strength of the 5000 Å thiocarbonyl absorption compared with that of the 3000 Å carbonyl absorption (Figs. 1 and 2). Other factors being equal, the dipole strength acquired by one transition from another is

[12] Moffitt, Woodward, Moscowitz, Klyne, and Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.
[13] Brutcher and Bauer, *J. Amer. Chem. Soc.*, 1962, **84**, 2236.
[14] Evans, *J. Chem. Phys.*, 1955, **23**, 1424.
[15] Labhart and Wagniere, *Helv. Chim. Acta*, 1959, **42**, 2219.
[16] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

inversely proportional to the square of the interval between the two transition energies.[17] The energy separation between the charge-transfer and the $n \rightarrow \pi^*$ transition of a saturated ketone is some 20,000 cm.$^{-1}$, but the interval between the corresponding transitions of a saturated thioketone is considerably larger, as the $n \rightarrow \pi^*$ absorption lies at an energy lower by 13,000 cm.$^{-1}$ and the charge-transfer excitation has a higher energy, since the thiocarbonyl group is a weaker electron-acceptor than the carbonyl group.

Experimental.—Materials. 3β-Hydroxy-5α-androstan-17-one was obtained commercially, and 3β-hydroxy-5α-androstane-17-thione was prepared by the method of Djerassi and Herbst.[9]

Absorption spectra. These were measured, for ethanol solutions, by means of an Optica double-beam grating spectrophotometer.

Circular-dichroism spectra. These were measured, for ethanol solutions, by means of the spectrophotometer previously described.[7]

[17] Herzberg and Teller, *Z. phys. Chem.*, 1933, *B*, **21**, 410.