A Simple Through-bond Approach to Optical Activity

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From an analysis of the molecular orbitals and transition moments of various molecular systems it is concluded that the change in rotatory strength of the n–π^* transition of a ketone is governed by a through-bond mechanism and that the controlling factor is the interaction between the substituent and the n,π orbital density as it appears at the substituted carbon atom. Using this method it is possible to understand not only those experimental results which are consistent with the Octant Rule, but also those which are anomalous to it.

THE Octant Rule, first suggested in the late 1950s,[1,2] was formally published in 1961 [3] in an attempt to relate the sign and magnitude of the Cotton effect of the n–π^* transition exhibited by a saturated ketone to the disposition of the atoms in space about the carbonyl chromophore. The rule was stated simply as: ' the sign of the contribution which a given atom at point P with cartesian co-ordinates x,y,z makes to anomalous rotatory dispersion will vary as the simple product $x\,.\,y\,.\,z$ '. The octants thus generated are shown in Figure 1.

Whilst in general this rule was valid it was noted that a fluorine atom usually gave a contribution opposite to that of substituents such as Me, Cl, or Br when placed in an equivalent position.[4]

Since its conception the Octant Rule has been the subject of a great deal of investigation both experimental and theoretical. The main controversy has concerned the shape or even the necessity of existence of the third surface dividing front and rear octants.[5-8] Quadrant Rules, where the Cotton effect of a substituent depends only on the product $x\,.\,y$ of the substituent, have been put forward where it is argued that from a group-theoretical point of view such rules are more fundamental.[9]

A theoretical study by Lynden-Bell and Saunders [10] concluded that for α-substituted ketones the effect of the substituent was transmitted through the intervening bonds rather than by direct interaction with the carbonyl orbitals. Following this, an analysis of the c.d. spectra of amino-ketones,[11] and γ- and δ-substituted ketones by Hudec and his co-workers [12,13] indicated that the interaction of substituent and carbonyl group in these molecules was controlled by a through-bond mechanism, and in addition that the ground state was more important than the excited state in determining chirality.

More recently both these observations have been confirmed by a molecular orbital analysis of the asymmetric nature of the n and π^* orbitals, as they

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[1] W. Moffitt and A. Moscowitz, *Abs. Papers Amer. Chem. Soc.*, 1958, **133**, 270.

[2] W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, 1959, **30**, 648.

[3] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.

[4] C. Djerassi and W. Klyne, *J. Amer. Chem. Soc.*, 1957, **79**, 1506.

[5] Y. H. Pao and D. P. Santry, *J. Amer. Chem. Soc.*, 1966, **88**, 4157.

[6] S. F. Mason, *Quart. Rev.*, 1963, **17**, 20; A. Rauk, O. Jarvie, H. Ichimura, and J. M. Barriel, *J. Amer. Chem. Soc.*, 1975, **97**, 5656; E. G. Hohn and O. E. Weigang, jun., *J. Chem. Phys.*, 1968, **48**, 1127.

[7] T. D. Bowman and D. A. Lightner, *J. Amer. Chem. Soc.*, 1976, **96**, 3145.

[8] C. Coulombeau and A. Rassatt, *Bull. Soc. chim. France*, 1971, 516; D. A. Lightner and D. E. Jackman, *J. Amer. Chem. Soc.*, 1974, **96**, 1938; D. A. Lightner and T. C. Chang, *ibid.*, p. 3015; D. A. Lightner and D. E. Jackman, *J.C.S. Chem. Comm.*, 1974, 344.

[9] J. A. Schellman and P. Oriel, *J. Chem. Phys.*, 1962, **37**, 2114; J. A. Schellman, *ibid.*, 1966, **44**, 55.

[10] R. M. Lynden-Bell and V. R. Saunders, *J. Chem. Soc. (A)*, 1967, 2016.

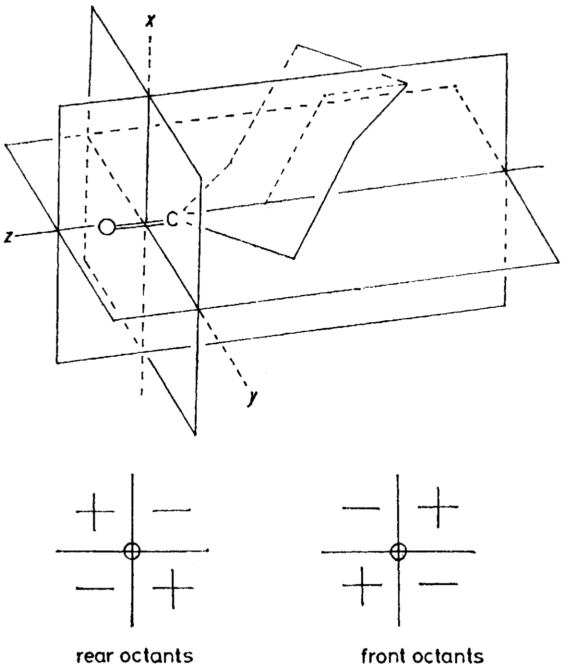
[11] J. Hudec, *Chem. Comm.*, 1970, 829; M. T. Hughes and J. Hudec, *ibid.*, p. 831.

[12] M. T. Hughes and J. Hudec, *Chem. Comm.*, 1971, 805.

[13] G. P. Powell and J. Hudec, *Chem. Comm.*, 1971, 806.

appear on the oxygen atom, of a variety of model ketones.[14,15]

As it is stated the Octant Rule implies that the Cotton effect of a substituent is independent of the nature of the skeleton connecting it and the carbonyl group. Consequently most previous theories have considered the direct through-space interaction of the substituent and the orbitals of the carbonyl chromophore. The type of rule generated by this method is critically dependent on the form of the orbitals chosen. This may be illustrated as follows.



rear octants front octants

FIGURE 1 The octants as proposed by the original Octant Rule

The rotatory strength R of the n–π^* transition of a ketone is given by equation (1) [16] where $\langle n|\mu_k|\pi^*\rangle$ is the

$$R = -Im\left\{\sum_{kj}^{x,y,z}\langle n|\mu_k|\pi^*\rangle\cdot\langle\pi^*|m_k|n\rangle\right\} \qquad (1)$$

electric transition moment, $\langle\pi^*|m_k|n\rangle$ is the magnetic transition moment, and $Im(a + ib) = b$.

Using the co-ordinate system of Figure 1, and for a symmetric molecule, the only non-zero term in equation (1) is $\langle\pi^*|m_z|n\rangle$. In order to make R non-zero it is necessary to mix in transitions $(p - q)$ with large $\langle p|\mu_z|q\rangle$ values. Such transitions are of the type π–π^*, n–π'^*, or n–$3d_{yz}$.

From perturbation theory the expression for R becomes (2) where $\lambda_i = \langle n|\mathscr{H}'|\psi_i\rangle\ (E_n - E_i)^{-1}$, $\lambda_j = \langle\pi^*|\mathscr{H}'|\Psi_j\rangle\ (E_{\pi^*} - E_j)^{-1}$, and $\mathscr{H}'$ is the perturbation Hamiltonian. Terms involving $\lambda_i\,.\,\lambda_j$ can be neglected.

The value of the total magnetic moment will be dominated by the value of $\langle\pi^*|m_z|n\rangle$ and consequently

$$R = -Im\Bigg\{\Bigg[\langle n|\mu_z|\pi^*\rangle + \sum_i^{\text{occ}}\lambda_i\langle\Psi_i|\mu_z|\pi^*\rangle + \sum_j^{\text{unocc}}\lambda_j\langle n|\mu_z|\Psi_j\rangle\Bigg]\times\Bigg[\langle\pi^*|m_z|n\rangle + \sum_i^{\text{occ}}\lambda_i\,\langle\pi^*|m_z|\Psi_i\rangle + \sum_j^{\text{unocc}}\lambda_j\langle\Psi_j|m_z|n\rangle\Bigg]\Bigg\} \qquad (2)$$

may be taken as constant for a particular system. That the magnetic moment can be taken as constant has been shown in many previous studies (*inter alia* refs. 5, 7, and 14).

The variation in the rotational strength of the n–π^* transition is then due to the variation of the final two terms of the electric moment in equation (2), the first term being zero.

If the perturbation causing the mixing of n with Ψ_i and π^* with Ψ_j is in all regions of space positive, then R is proportional to the orbital ' transition ' densities $n\,.\,\Psi_i$ and/or $\pi^*\,.\,\Psi_j$. The type of sector rule then generated depends on the forms of the orbitals n, Ψ_i, π^*, and Ψ_j.

Examples.—(i) $n = (\Phi_y)^0$, $\Psi_i = \pi = C_\pi^0(\Phi_x)^0 + C_\pi^c(\Phi_x)^c$, $\lambda_j = 0$. In this case the product $n\,.\,\pi$ generates a quadrant rule for R. The mixing in of π into n in this manner was first suggested by Wagnière.[17]

(ii) If the n orbital is allowed to delocalize onto the carbon atom of the carbonyl group,[18] and taking $\Psi_i = \pi$, then the orbitals are: $n = C_n^0(\Phi_y)^0 - C_n^c(\Phi_y)^c$, $\pi = C_n(\Phi_x)^0 + C_ç^c(\Phi_x)^c$, and $\lambda_j = 0$.

The product $n\,.\,\pi$ now generates an Octant Rule with the position of the third nodal plane (xy), cutting through the delocalized n orbital determined by the relative magnitudes of C_n^0 and C_n^c.

(iii) $n = (\Phi_y)^0$, $\lambda_i = 0$, $\Psi_j = C_{dyz}^0(\Phi_{dyz})^0 + C_{dyz}^c(\Phi_{dyz})^c$. The mixing in of the $3d_{yz}$ orbitals of the C and O atoms of the carbonyl group, as suggested by Moscowitz,[16] gives rise to an Octant Rule.

Although the mixing in of $3d$ orbitals produces an Octant Rule it is not a prerequisite for producing those results which are consistent with it. This is illustrated by the complete calculation of R using wavefunctions obtained from such methods as CNDO [5,7] or extended Hückel.[19] In these methods it is possible to obtain results consistent with the Octant Rule *without* the inclusion of *d* orbitals. The main feature of this latter type of calculation is that there is no *a priori* constraint on the localization of any of the orbitals.

It was decided to examine in detail the various components of equation (2). The molecular orbitals were calculated using the CNDO/2 method [20] and the transition moments obtained from the one-centre formalism of Pao and Santry.[5] From an analysis of four molecular

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[14] E. E. Ernstbrunner, M. R. Giddings, and J. Hudec, *J.C.S. Chem. Comm.*, 1976, 953; M. R. Giddings, E. E. Ernstbrunner, and J. Hudec, *ibid.*, pp. 954, 956.

[15] M. R. Giddings, Ph.D. Thesis, Southampton, 1976.

[16] A. Moscowitz, *Adv. Chem. Phys.*, 1962, **4**, 67.

[17] G. Wagnière, *J. Amer. Chem. Soc.*, 1966, **88**, 3937.

[18] T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, 1968, **48**, 3115.

[19] R. Gould and R. Hoffmann, *J. Amer. Chem. Soc.*, 1970, **92**, 1813.

[20] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.

systems the following conclusions with regard to equation (2) were drawn.

(a) The complete term $\sum_{j} \lambda_j \langle n|\mu_z|\psi_j\rangle$ can be neglected in most instances, principally because λ_j is very small in comparison to λ_i. This is in agreement not only with the conclusion of Bowman and Lightner [7] who found that the π^* orbital is almost completely localized on the carbonyl group and remains virtually unaffected by substitution, but also with the empirical observation that the asymmetric character, with respect to the *xz* plane, of the π^* orbital as it appears on the oxygen atom (measured by θ_{π^*}) is also virtually constant irrespective of substitution.[14]

(b) The term $\sum_{i}^{\text{occ}} \lambda_i \langle \Psi_i|\mu_z|\pi^*\rangle$ can be replaced by a single term $\lambda_{\pi_1}\langle\pi_1|\mu_z|\pi^*\rangle$ where π_1 is the highest occupied π molecular orbital of the system. There are two reasons for this: (i) λ_i for π orbitals other than π_1 is relatively small (due to $E_n - E_\pi$ being large), and (ii) $\langle\pi_i|\mu_z|\pi^*\rangle$ for $i \neq 1$ is in most cases negligible. The expression of R then reduces to $R = -Im\{\lambda\pi_1 \langle\pi_1|\mu_z|\pi^*\rangle \langle\pi^*|m_z|n\rangle\}$. Further it was also noted that the n and π_1 orbitals in our calculations are *delocalized over the whole molecule*. Thus, with both the n and π_1 orbitals delocalized the density $n\,.\,\pi_1$ probes the entire molecule and a through-bond mechanism becomes viable for the induction of optical activity. In such a mechanism it is expected that the largest perturbation causing orbital mixing, and hence optical activity, will arise from the substituted centre. Considering the substituted carbon atom only (C_s), then the n and π_1 orbitals as they appear at this atom can be written:

$$n = \alpha\Phi_x + \beta\Phi_y + \gamma\Phi_z + \delta\Phi_{H_1} + \varepsilon\Phi_{H_2} + \eta\Phi_{H_3}$$
$$\pi_1 = \alpha'\Phi_x + \beta'\Phi_y + \gamma'\Phi_z + \delta'\Phi_{H_1} + \varepsilon'\Phi_{H_2} + \eta'{}_{H_3}$$
(Greek characters = AO coefficients)

On substituting these orbitals into the equation for λ_i and if the perturbation ($\mathscr{H}'$) is allowed to operate only on the hydrogen atoms then: $\lambda_{\pi_1} \simeq \{\delta\delta' \langle\Phi_{H_1}|\mathscr{H}'|\Phi_{H_1}\rangle + \varepsilon\varepsilon' \langle\Phi_{H_2}|\mathscr{H}'|\Phi_{H_2}\rangle + \eta\eta' \langle\Phi_{H_3}|\mathscr{H}'|\Phi_{H_3}\rangle\} (\Delta E)^{-1}$ (terms between different hydrogen atoms are neglected).

For a given system ΔE ($= E_n - E_\pi$) is constant and for a constant perturbation then λ_{π_1} for perturbing a *single* hydrogen atom (H_p) can be written $\lambda_{\pi_1} \simeq KC_n{}^{H_p}\,.\,C_\pi{}^{H_p}$ where $K = \langle\Phi_{H_p}|\mathscr{H}'|\Phi_{H_p}\rangle (\Delta E)^{-1}$ and $C_n{}^{H_p}$ and $C_\pi{}^{H_p}$ are the AO coefficients of the hydrogen atom H_p in the n and π orbitals respectively.

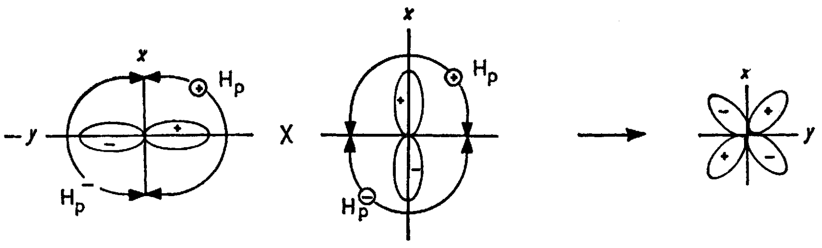
Thus R now can be written as in equation (3).

$$R = -KC_n{}^{H_p}\,.\,C_\pi{}^{H_p}\, Im\{\langle\pi_1|\mu_z|\pi^*\rangle \langle\pi^*|m_z|n\rangle\} \quad (3)$$

Throughout the following discussion K is taken as positive.

The nature of the interaction (bonding or anti-bonding) between the hydrogen atoms and the various p orbitals of the substituted carbon atom can be used to define a surface at each atom. If the interaction between the hydrogen atom and each p orbital is *always bonding* then the surface $n\,.\,\pi_1$ generated can be illustrated as in the Scheme, *i.e.* the product $n\,.\,\pi_1$ varies as $S_{H/p_x}\,.\,S_{H/p_y}$, where S_{H/p_t} is the overlap integral between the hydrogen atom and the p_t AO of C_s.

The product $n\,.\,\pi_1$ then divides the region of space around *each carbon atom* into quadrants. It is these *local* quadrants which determine the sign of the contribution which a given atom makes to ΔR.



p_y AO at C_s (n orbital) p_x AO at C_s (π_1-orbital)   Variation of $n.\pi_1$ with H position

SCHEME

We now apply equation (3) to the various systems of Figure 2.

Acetone (A).—The n and π_1 orbitals are illustrated in Figure 3, and the calculated transition moments are $\langle\pi_1|\mu_z|\pi^*\rangle = 1.40$ and $\langle\pi^*|m_z|n\rangle = 0.54$. Substitution into equation (3) yields contributions of $+9.93$ from H_6 and H_9, -9.93 from H_5 and H_{10}, and zero from H_4 and H_8.*

Examining in more detail the orbitals as they appear at C_1, then the π_1 orbital is represented by a pure p_x AO, and the n by a combination of a p_y and a p_z AO. This latter combination can be replaced by a resultant p orbital of magnitude $[(C_n{}^{c_1})_z{}^2 + (C_n{}^{c_1})_y{}^2]^{1/2}$ and direction θ with respect to the x axis $\{\theta = \tan^{-1}[(C_n{}^{c_1})_z/(C_n{}^{c_1})_y]$, see Figure 4$\}$. For a constant perturbation the space around C_1 is divided into quadrants; the quadrants being generated by the prodjct $n\,.\,\pi_1$. This is represented in Figure 5.

With both the electric and magnetic transition moment positive R is proportional to $-n\,.\,\pi_1$. Thus, for ΔR; relative to C_1, H_{10} is in a *negative* quadrant and H_9 in a positive one. The same procedure at C_2 gives H_5 in

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* All values of the contribution quoted are $\times 10^2$ a.u.$^{-1}$.

a negative quadrant and H_6 in a positive one. It is then the perturbation of these local quadrants which control the overall sign of ΔR.

Cyclohexanone (*B*).—The n and π_1 orbitals are given in Figure 6. In this molecule the π_1 orbital is split by a σ_z orbital to give π_{1a} and π_{1b}. Since the energy splitting between π_{1a} and π_{1b} is small, of the order of 0.6 eV, then both these π orbitals must be considered. The calculated transition moments are: $\langle\pi_{1a}|\pi_z|\pi^*\rangle = +0.98$, $\langle\pi_{1b}|\mu_z|\pi^*\rangle = +0.73$, and $\langle\pi^*|m_z|n\rangle = +0.54$.

TABLE 1

Contributions to R from the hydrogen atoms of cyclohexanone

Transition	α-Axial	α-Equatorial	β-Axial	β-Equatorial
π_{1a}–π^*	+1.45	+12.455	+1.35	−22.60
π_{1b}–π^*	+8.44	−14.37	+8.44	+15.40
Total	+9.89	−1.91	+9.79	−7.20

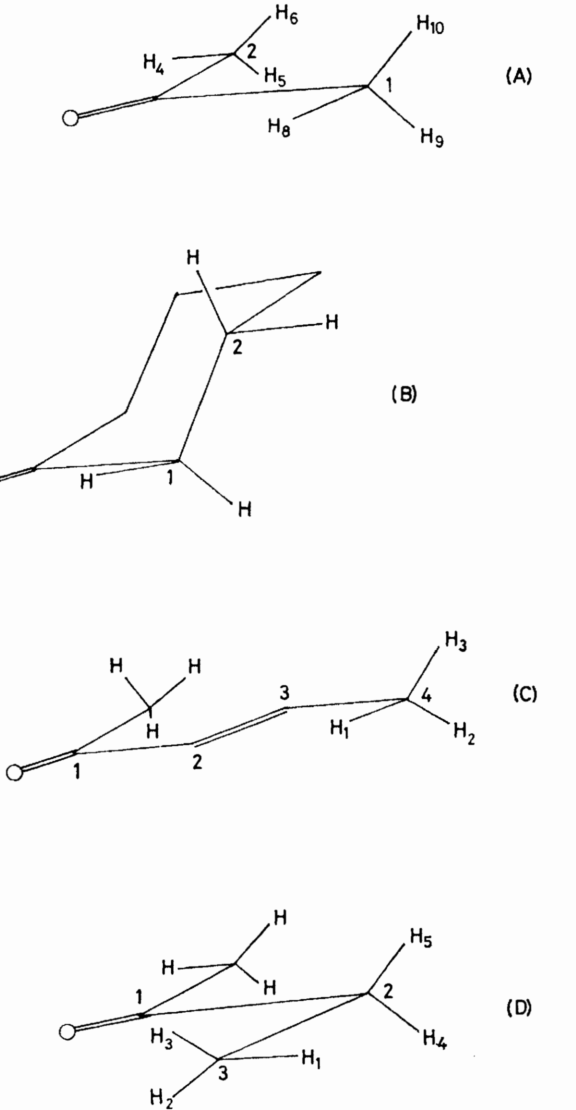

FIGURE 2 Model systems: tetrahedral angles 109.47°, trigonal angles 120.0°; C_{sp^3}–H 1.09, C=O 1.23, OC–C_{sp^3} 1.52, C=C 1.34, C_{sp^3}–C_{sp^3} 1.54, C_{sp^2}–H 1.08 Å

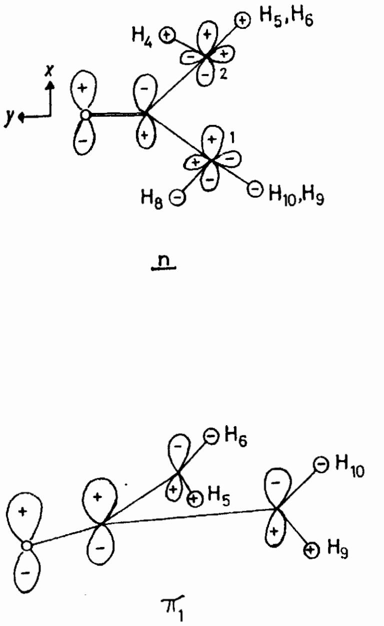

FIGURE 3 The n and π_1 orbitals of acetone

With the same procedure as before the calculated contributions to rotatory strength are given in Table 1.

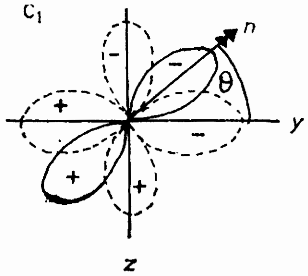

FIGURE 4 The n orbital of acetone at C_1: θ = 25.6°; ⟶ represents direction of negative lobe of p orbital

The total prediction by this method is that the β-axial and β-equatorial positions when substituted should give rise to opposite signs of rotatory strength. This is experimentally observed in the β-substituted adamantanones[21] (1).

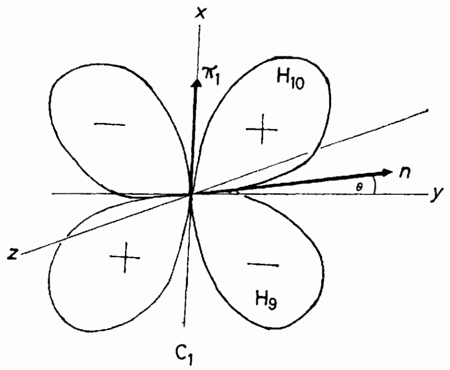

FIGURE 5 The product $n \cdot \pi_1$ at C_1 of acetone

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[21] G. Snatzke and G. Eckhardt, *Tetrahedron*, 1968, **24**, 4543; G. Snatzke, B. Ehrig, and H. Klein, *ibid.*, 1969, **25**, 5601. The results quoted are in 95% ethanol.

In a manner analogous to that of acetone the region of space about each carbon atom is divided into quadrants by the product $n \,.\, \pi_1$. (For a simple representation $\pi_1 = \pi_{1a} + \pi_{1b}$.) The orbitals as they appear at C_2 are given in Figure 7.

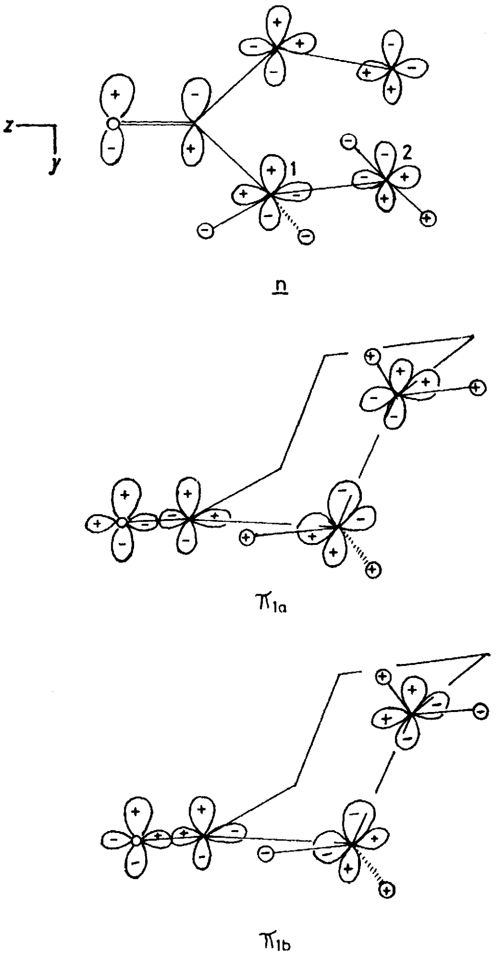
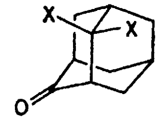


FIGURE 6 The n and π_1 orbitals of cyclohexanone

γ-Substituted αβ-Unsaturated Ketone (C).—The geometry of this model was such that C_1—C_4 and H_1 were all in the zy planes. It was found that important contributions could be expected only from the π_1 orbital. The transition moments are: $\langle \pi_1 | \mu_z | \pi^* \rangle = 1.83$ and $\langle \pi^* | m_z | n \rangle = 0.23$. From equation (3) the contributions to R on perturbing H_2 or H_3 are −23.03 and +25.88 respectively. The orbitals are illustrated in Figure 8.



(1)

Thus substituting H_2 should, by this method, yield a negative rotatory strength. In acetone the substitution of H_9 should yield a positive rotatory strength. According to the Octant Rule both H_9 of acetone and H_2 of the αβ-unsaturated ketone are in the *same* positive octant and should therefore yield the same sign of contribution to R. The experimental results for the 6β-substituted Δ^4-3-ketosteroids (2)[22] are in agreement with our prediction. The results are summarized in Table 2 with the results for the α-axial-substituted ketones taken from compound (3).[23]

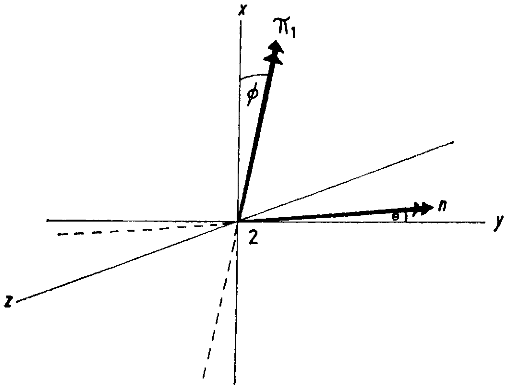


FIGURE 7 The n and π_1 orbitals of cyclohexanone at C_2: $\pi_1 = \pi_{1a} + \pi_{1b}$; ⟶ represents direction of positive lobe of p orbital

TABLE 2

Comparison of predicted and observed Cotton effects in the α-axial substituted ketone (3) and the 6β-substitued αβ-unsaturated ketone (2)

	(3)		(2)	
	Me	Cl	Me	Cl
Experimental δΔε	+1.23	+3.44	−1.8	−1.9
Predicted, Octant Rule	+	+	+	+
Predicted, this method	+	+	−	−

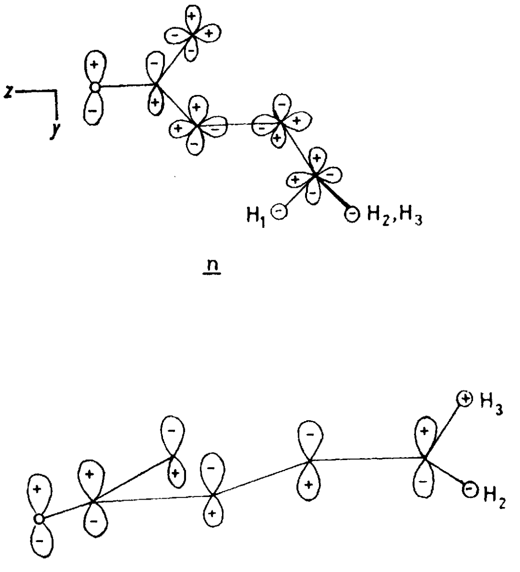


FIGURE 8 The n and π_1 orbitals of the αβ-unsaturated ketone (C)

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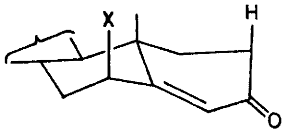
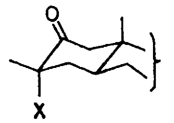
[22] K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *Tetrahedron Letters,* 1968, 1661.

[23] G. P. Powell, Ph.D. Thesis, Southampton, 1972.

The variation in the Cotton effect of the n–π^* transition in the γ-substituted $\alpha\beta$-unsaturated ketones was originally attributed to conformational changes in ring A;[24] the effect of the substituent being to reverse the chirality of the ring. However, such changes have been criticized on the basis of n.m.r. evidence.[25] Assuming no conformational changes on substitution the c.d. spectra of these compounds have been rationalized in terms of the contributions of the pseudoaxial bonds on the α' and γ carbon atoms.[26]



(2)



(3)

'Front Octant' Ketone (D).—In order to determine whether our method was capable of reproducing 'front octant' effects a model system (D) with the geometry of Figure 2 was examined. Atoms C_1—C_3 and H_1 are all in the zy plane. The important orbitals were again the n and π_1 and are illustrated in Figure 9. The calculated transition moments are: $\langle\pi_1|\mu_z|\pi^*\rangle = 0.81$ and $\langle\pi^*|m_z|n\rangle = 0.48$. From equation (3) the contributions to R are: $H_3 = +30.45$, $H_2 = -30.45$, $H_5 = -38.90$, and $H_4 = +38.9$.

The quadrants generated by the product $n\,.\,\pi_1$ at C_2 and C_3 are shown in Figure 10. Thus the perturbation of H_5 should give the opposite sign of rotatory strength to the perturbation of H_3. In terms of the Octant Rule[3] this is equivalent to the crossing of the xy plane.

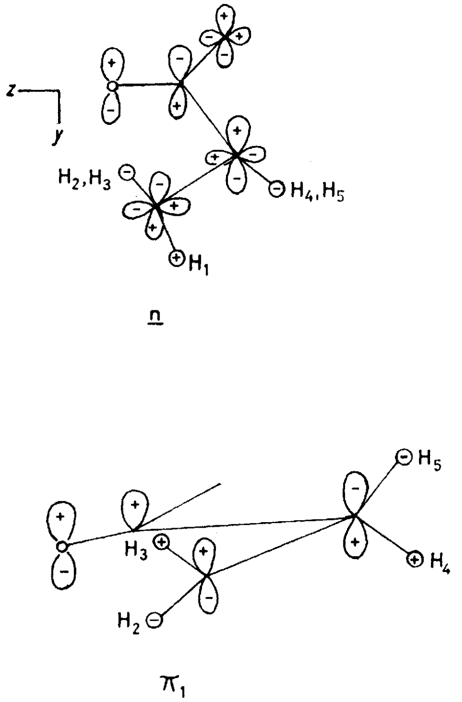


FIGURE 9 The n and π_1 orbitals of the 'front octant' ketone (D)

Conclusions.—The conclusions may be summarized as follows.

(i) The main contribution to optical activity arises from the ground state. This agrees with the conclusions reached in refs. 12—14.

(ii) The mixing in of the orbitals to induce optical activity is controlled by the substituted centre.

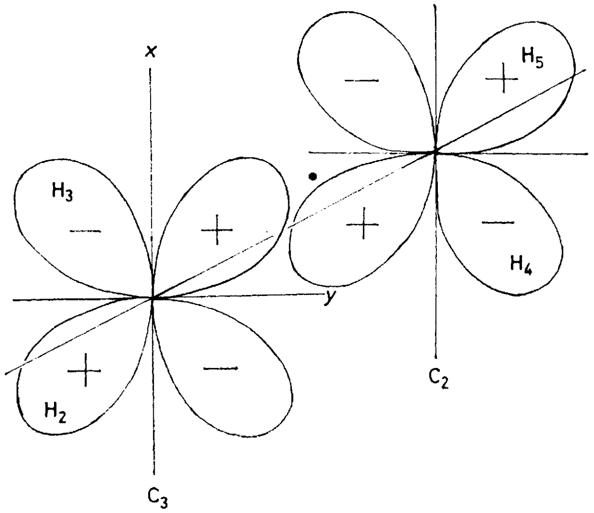


FIGURE 10 The local quadrants generated by the product $n\,.\,\pi_1$ at C_2 and C_3 of the 'front octant' ketone (D)

(iii) The sign of the product $n\,.\,\pi_1$ at any centre is a function of the nodal properties of the n and π_1 orbitals, and these in turn are a function of the geometry of the molecular framework.

In a given molecule the relative sign and magnitude of the contribution made by a perturbing atom to the rotatory strength is a function of λ_{π_1}. Likewise λ_{π_1} also controls the nature of the resultant n orbital (n'), *i.e.* $n' = n + \lambda_{\pi_1}\,.\,\pi_1$ (where n and π_1 are the original unperturbed n and π_1 orbitals respectively).

If we consider the resultant n' orbital as it appears at the oxygen atom of the carbonyl group, then in addition to its large y component $(C_n^0)_y$ it will also contain a small x component $(C_n^0)_x$. It would be expected for $(C_n^0)_x$ to reflect the sign and magnitude of λ_{π_1}. That is to say, the effect of the perturbation at the substituted centre, measured by λ_{π_1}, is 'transmitted' through the intervening skeleton where its result is measured by $(C_n^0)_x$.

The two MO coefficients $(C_n^0)_y$ and $(C_n^0)_x$ can then be used as a measure of λ_{π_1} and hence of the optical activity induced by a perturbation.

The n' orbital as it appears at the oxygen atom of the carbonyl group has been investigated by Hudec *et al.*,[14,15] where the technique adopted was to take $\tan\theta_n = (C_n^0)_x/(C_n^0)_y$ as a measure of the asymmetry of the n' orbital.

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Using CNDO/2 calculations on a variety of model systems it was found that the sign and magnitude of the contribution a substituent makes to the rotatory strength of the n-π^* transition was proportional to $-\Delta\Theta_n$. [$\Delta\Theta_n = \Theta_n(X = X) - \Theta_n(X = H)$; X = substituent]. Using the molecular orbitals of acetone (Figure 3), if λ_{π_1} is positive then also is Θ_n; conversely if λ_{π_1} is negative then so is Θ_n.

In our CNDO/2 calculations we employed the usual minimal basis set, *i.e.* a 1s orbital for hydrogen, and a 2*s* and three 2*p* orbitals for carbon and oxygen. The conclusions in this work are therefore only valid as long as this basis set is valid for the system under consideration. The justification for the CNDO/2 method with this basis set is that in the past it has been shown (*inter alia* refs. 7, 5, and 14) to be successful in predicting the rotatory strengths of a variety of molecules.

The electronic transitions of carbonyl compounds higher in energy than the n-π^* excitation that have been especially characterized are all to Rydberg states (n-3s, n-3p, n-3d) with the π-π^* transition lying at an even higher energy.[27] However, for the Rydberg states to be important in determining the *rotational strength* of the n-π^* transition there must be a non-zero matrix element between the π^* and the Rydberg orbital, *i.e.* λ_j must be non-zero.

There are essentially two ways by which λ_j can be made appreciable, by a through-bond mechanism or by a through-space mechanism.

For the through-bond mechanism to be viable the π^* orbital must have non-zero molecular orbital density at the substituted centre. The extensive calculations (using the CNDO/S method) by Bowman and Lightner [7] have shown that whilst the n orbital is highly delocalized over the whole molecule the π^* orbital is *not*. Their calculations give almost 94% of the π^* orbital localized on the C=O group with the only other contributions of any size coming from the α positions. Thus, provided these calculations are reflecting the true situation, a through-bond mechanism for the mixing of the π^* orbital with other orbitals is unlikely.

It was also shown [7] that the π^* orbital changed very little from molecule to molecule. This suggests that there is no through-space effect acting on the π^* orbital. Thus even if the substituent has a non-zero interaction with the Rydberg orbitals it will have little effect upon the mixing of the π^* and Rydberg orbitals.

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