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A Molecular Orbital Theory of Optical Rotatory Strengths of Molecules

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Abstract: An approximate self-consistent field molecular orbital theory has been applied to the calculation of the molecular orbital of cyclohexanone and some of its methyl derivatives. The predicted first excited state, corresponding to the excitation of an electron from the highest filled to the lowest unoccupied molecular orbital, was found to correspond very closely to the expected carbonyl $n \rightarrow \pi^*$ transition. However, the highest filled orbital was not a pure oxygen lone-pair orbital, but had a significant admixture of 2p orbital from the adjacent carbon atom. The calculated point of intersection of the π^* nodal surface, with the carbon-oxygen bond, was found to agree well with Moffitt's original estimate of the position of plane C of the octant rule. A semiquantitative molecular orbital theory of optical rotatory strengths, based on the neglect of all two-center integrals, was also developed, this latter approximation being consistent with the neglect of differential overlap used to calculate the above wave functions. The theory yielded reasonable magnitudes for the rotatory strengths, the signs agreeing with the octant rule in all but one case. The calculated magnetic moment remained sensibly constant for the carbonyl $n \rightarrow \pi^*$ transition in all the molecules studied. On breaking down the electric transition moment into atomic contributions, it was found to be largely localized in the carbonyl group, with important contributions from the carbon of the methyl group and the proton left "unpaired" by the substitution.

This paper reports on a self-consistent field molecular orbital (SCF MO) theory investigation of the optical rotatory strengths of molecules. The approximate SCF MO scheme used in this study is described in the next section and the expression for the optical rotational strength in this formulation is derived later. The method is applied to a calculation of the rotational strengths of methyl-substituted cyclohexanones and the results are described and discussed. In the remainder of this section we review briefly previous related work.

It is known that although Rosenfeld² gave the correct quantum mechanical result for the optical rotatory dispersion of molecules in 1929, very little use could be made of it for some time in the absence of quantum mechanical descriptions of molecules. Discussions of the relationship between optical rotatory strengths and chemical structure were almost entirely in terms of coupled oscillators,³ and, until the work of Condon,⁴ it was not clear whether it was necessary in simple theories to always strive for a description in terms of coupled oscillators. Condon showed that a single electron in a dissymmetric potential could indeed exhibit optical rotation.

Although the coupled oscillator and one-electron theories manifestly attempt to describe the one and same phenomenon, they start from different initial descriptions and emphasize different features of the

chemical structure of molecules. The coupled oscillator picture, and to a lesser extent the polarizability theories deriving from it, may be appropriate when the molecule is clearly recognizable in terms of a stable array of known oscillators or polarizable groups. The only additional feature to be added is the fact that these otherwise independent groups interact with each other as they interact with light. If indeed all this were true then it should be possible to understand the optical rotatory dispersion of complex molecules in terms of the known optical properties of the simpler constituent groups. In addition to the work of Kuhn,^{3,5a} the studies of Moffitt, Kirkwood, Tinoco, and others for polypeptides and polynucleotides are certainly in this tradition.^{5b} The one-electron model is more appropriate if one or more transitions of a particular chromophore are well removed in wavelength for all other transitions, and, as this particular chromophore is studied in different molecules, the effects of the substituents can be estimated in gross terms in the nature of perturbations on the otherwise known symmetry of the particular electron in question. Work on coordination compounds in general,⁶ the calculation of Moscovitz for the $n \rightarrow \pi^*$ transition of the carbonyl group,⁷ and the entire scheme of Kauzman, *et al.*,⁸ are in this latter tradition, which is useful whenever the stated conditions are met.

It is desirable to formulate yet another different

(1) (a) Bell Telephone Laboratories, Inc.; (b) Carnegie Institute of Technology. A major part of the work reported here was carried out during Dr. Santry's stay at the Bell Telephone Laboratories during the summer of 1965.

(2) L. Rosenfeld, *Z. Physik*, **52**, 161 (1929).

(3) A particularly good review of this type of approach is contained in the book by T. M. Lowry, "Optical Rotary Power," Longmans, Green and Co., London, 1935. Reprints are obtainable from University Microfilms, Ann Arbor, Mich.

(4) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).

(5) (a) W. Kuhn, *Ann. Rev. Phys. Chem.*, **9**, 417 (1958); (b) I. Tinoco, Jr., *Advan. Chem. Phys.*, **4**, 113 (1962).

(6) R. G. Wilkins and M. J. G. Williams, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 175.

(7) A. Moscovitz, *Advan. Chem. Phys.*, **4**, 97 (1962).

(8) W. J. Kauzman, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).

approximate description of the optical rotatory strength of molecules, and this is the concern of the present discussion. The present approach consists of adopting a sufficiently simple self-consistent field molecular orbital procedure so that approximate but *a priori* quantum mechanical descriptions of fairly complex molecules may be obtained. It is intended that this third type of study will supplement the former approaches. In particular we would be able to indicate in what cases changes in conformation result not only in the altered geometry of interactions between known transitions but also in the intrinsic nature of the oscillators themselves. With respect to the one-electron type of theory, we would guess that quite often the wave functions of chromophoric groups in molecules are not localized but are spread out over large portions of the molecule to different degrees depending on the nature of substituents. Therefore it is useful to know whether the role of a substituent is more than merely the presence of a group of incompletely shielded nuclei acting as an electrostatic perturbation as is the case, for example, in the calculations of Moscowitz. In all, the philosophy of the present study is not that every molecule must be studied, *a priori*, by itself as a special case. The objective is instead to help correlate and understand the areas of validity of the results of previous studies and to follow up on uninvestigated areas as they are delineated.

Finally, we point out that the rotational strengths referred to are the over-all electronic rotational strengths of a particular transition and, to the order of approximation contemplated, the distribution of the circular dichroism in the region of absorption would be the same as that of the ordinary absorption curve.⁹

Approximate Self-Consistent Field Molecular Orbital Scheme

As the approximate self-consistent field molecular orbital (SCF MO) scheme used in the present calculations has been described in detail elsewhere,^{10,11} it will only be briefly discussed here.

Molecular orbital theory¹² approximates the molecular electronic wave function to a suitable (antisymmetrized) product of one-electron orbitals

$$\Psi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \cdots & \psi_{N/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & & \vdots \\ \vdots & \vdots & \cdots & \vdots \\ \psi_{N/2}(N)\beta(N) & & & \end{vmatrix} \\ = |\psi_1\bar{\psi}_1\psi_2 \cdots \psi_{N/2}\bar{\psi}_{N/2}| \quad (1.1)$$

where Ψ_0 is the ground-state N -electron wave function, ψ_i is the i th molecular orbital, and α and β are spin functions. In all practical applications the molecular orbitals have to be further approximated to linear combinations of atomic orbitals (LCAO)

$$\psi_1 = \sum_{\mu} \chi_{\mu} C_{\mu 1} \quad (1.2)$$

where $C_{\mu i}$ is the coefficient of the μ th atomic orbital χ_{μ} in the i th molecular orbital. (Throughout the remainder of the paper Greek suffices will be reserved

for atomic and Roman for molecular orbitals.) For a molecule composed of protons and first-row atoms, we use a limited basis set of atomic orbitals consisting of four (Slater) orbitals ($2s$, $2p_x$, $2p_y$, $2p_z$) centered on each first-row atom, and one $1s$ orbital on each proton. The coefficients $C_{\mu i}$ together with the orbital energies ϵ_i are obtained as the solutions to a set of simultaneous self-consistent field (SCF) equations.¹³ The ones we use in the present theory are approximate not only because of the use of the LCAO approximation and a limited basis set but because of further approximations brought on by our adoption of neglect of differential overlap. In this further approximation all overlap integrals are neglected, together with all electron-repulsion integrals dependent upon overlapping charge distributions. These approximations greatly simplify the calculation by eliminating the difficult electron-exchange integrals, and, hopefully, the errors incurred from the two approximations cancel.¹³ With this simplification it is then practical to calculate approximate SCF wave functions for large molecules of arbitrary symmetry.

The details of how the scheme is made invariant with respect to the directions chosen for the $2p$ orbitals, how some of the matrix elements for Hamiltonian for the "core" electrons are obtained from atomic spectra, and how the nondiagonal matrix elements are taken to be proportional to overlap integrals are all discussed in ref 11 and need not be repeated here.

In addition to the molecular orbitals used to construct the ground-state wave function, the solution to the SCF equations yields extra molecular orbitals which may be used to construct approximate excited-state wave functions.¹⁴ The singlet excited-state wave function corresponding to the excitation of an electron from the i th filled to the j th unoccupied molecular orbital is given by

$$\Psi_{i \rightarrow j} = \frac{1}{\sqrt{2}} \{ |\psi_1\bar{\psi}_1\psi_2 \cdots \psi_i\bar{\psi}_j| + |\psi_i \cdots \psi_j\bar{\psi}_i \cdots| \} \quad (1.3)$$

The approximate ground-state wave function (1.1) and excited-state wave function (1.3) will now be used to develop a molecular orbital theory of optical rotatory strengths.

Strictly speaking, the excited states should be obtained from separate SCF calculations, but it is not known that this approximate molecular orbital theory is appropriate for open-shell calculations for excited states and at this time we prefer to construct the excited states in the manner indicated.

LCAO MO Theory of Optical Rotatory Strengths

Although the angle of rotation at a given wavelength is the most directly observable property characterizing the optical activity of a molecule, it is not suitable for the present study as it requires the calculation of the excitation energies of the various molecular excited states which are not easily calculated using approximate molecular orbital schemes of the type described above. For this reason we develop instead a theory of optical rotatory strengths. The so-called reduced optical

(9) H. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

(10) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, 129 (1965).

(11) J. A. Pople and G. A. Segal, *ibid.*, **43**, 136 (1965).

(12) C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1961)

(13) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(14) H. L. McMurray and R. S. Mulliken, *Proc. Natl. Acad. Sci. U. S.*, **26**, 312 (1940).

rotatory strength of a transition from the ground-state O of a molecule to its s th excited state is given by⁷

$$[R_{0s}] = \frac{100}{\beta D} \text{Im} \langle \Psi_0 | \mu | \Psi_s \rangle \cdot \langle \Psi_s | M | \Psi_0 \rangle \quad (2.1)$$

where β and D are, respectively, the Bohr magneton and the Debye, Ψ_0 and Ψ_s are the molecular wave functions for the ground and s th excited states; μ is the electric dipole operator

$$\mu = \sum_i e_i r_i$$

i is summed over all charged particles in the molecule, M is the angular momentum operator

$$M = \sum_i m_i$$

and Im means the imaginary part in the sense of

$$\text{Im}(a + ib) = b$$

Although until very recently quantitative data for rotational strengths were difficult to determine experimentally, Moscovitz⁷ has obtained values for the $n \rightarrow \pi^*$ transition in the carbonyl group of several cyclic ketones.

If we now approximate Ψ_0 to the ground-state wave function (1.1) and Ψ_s to the excited-state molecular orbital wave function (1.3), the molecular orbital approximation to the rotatory strength is found to be

$$[R_{ij}] = 200a_0 \text{Im} \langle \psi_i | r | \psi_j \rangle \cdot \langle \psi_j | m | \psi_i \rangle \quad (2.2)$$

where a_0 is the Bohr radius, $\langle \psi_i | r | \psi_j \rangle$ is in atomic units, and $\langle \psi_j | m | \psi_i \rangle$ is in units of \hbar . One foreseeable difficulty in the application of (2.3) is that in general the orbitals ψ_i and ψ_j corresponding to a given spectral system will not be known. On the other hand, a successful theory of rotatory strengths may prove useful in the assignment of these orbitals. In the present calculations, on the carbonyl 290-m μ system in the cyclohexanones, this difficulty does not arise, because, as we shall see later, the predicted first excited state agrees very well with the accepted $n \rightarrow \pi^*$ description¹⁴ of the carbonyl 290-m μ system.

On expanding the MO's as linear combination of atomic orbitals, the electric and magnetic transition moments between orbitals ψ_i and ψ_j are given as a sum of one- and two-center integrals. In the approximate theory developed here, only the one-center integrals, that is, integrals involving two atomic orbitals on the same center, are retained. Although this approximation appears drastic, it is consistent with the neglect of all overlap charge distributions in the SCF scheme used to calculate the molecular orbitals. Further, this approximation has been used successfully to develop a useful theory of magnetic susceptibilities and chemical shifts.¹⁵ The electric moment in this approximation is expressed as the sum of atomic contributions

$$\langle \psi_i | r | \psi_j \rangle = \sum_A \left\{ \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu j} \int \chi_{\mu} r \chi_{\nu} dz \right\} \quad (2.3)$$

where the summation over A includes all the atoms in the molecule, and the summations over μ and ν are over all the orbitals centered on A . In the case of A being a proton, μ and ν only take one value correspond-

ing to the 1s orbital of that proton; otherwise μ and ν range over the four atomic orbitals 2s, 2p_x, 2p_y, and 2p_z. The integral over atomic orbitals in eq 2.3 is calculated by expression r as the sum of the position vector R_A of the atom A , on which μ and ν are centered, and a local vector r_A referred to local axes centered on A (eq 2.4)

$$\int \chi_{\mu} r \chi_{\nu} dz = R_A \int \chi_{\mu} \chi_{\nu} dz + \int \chi_{\mu} r_A \chi_{\nu} dz \quad (2.4)$$

The first integral vanishes unless $\mu = \nu$ because the atomic orbitals on a given center are mutually orthogonal, and the second integral vanishes unless the pair of orbitals μ and ν comprise a 2s and 2p orbital. The last integral in eq 2.4 is the local atomic dipole moment η_A of atom A , where

$$\eta_A = \int \chi_{2s} x \chi_{2p_x} d\tau = \int \chi_{2s} y \chi_{2p_y} d\tau = \int \chi_{2s} z \chi_{2p_z} d\tau \quad (2.5)$$

The molecular transition moment is then given by

$$\langle \psi_i | r | \psi_j \rangle = \sum_A \left[\left\{ \sum_{\mu} C_{\mu i} C_{\mu j} R_A \right\} + \left\{ C_{sA_i} C_{x_{Aj}} + C_{xA_i} C_{sA_j} \right\} \mathbf{x} + \left\{ C_{sA_i} C_{y_{Aj}} + C_{yA_i} C_{sA_j} \right\} \mathbf{y} + \left\{ C_{sA_i} C_{z_{Aj}} + C_{zA_i} C_{sA_j} \right\} \mathbf{z} \right] \eta_A \quad (2.6)$$

where \mathbf{x} , \mathbf{y} , and \mathbf{z} are unit vectors in the x , y , and z direction, and C_{sA_i} , C_{xA_i} , and the coefficients of the 2s and 2p_x orbitals centered A in the i th molecular orbital. In this simple theory, the electric transition dipole moment is given as the sum of the dipole moment of the transition charge densities in each atom and the local atomic transition moments.

Similarly, on expanding the magnetic transition moment and neglecting all two-center terms

$$\langle \psi_j | m | \psi_i \rangle = -i \sum_A \left\{ \sum_{\mu} \sum_{\nu} C_{\mu j} C_{\nu i} \int \chi_{\mu} (\mathbf{r} \times \nabla) \chi_{\nu} dz \right\} \quad (2.7)$$

in units of \hbar

$$\int \chi_{\mu} (\mathbf{r} \times \nabla) \chi_{\nu} dz = R_A \int \chi_{\mu} \nabla \chi_{\nu} dz + \int \chi_{\mu} (\mathbf{r}_A \times \nabla) \chi_{\nu} dz \quad (2.8)$$

The first integral is related to the local atomic transition moment integral (2.5) and also vanishes unless χ_{μ} and χ_{ν} correspond to a 2s and 2p orbital. The second integral is simply the local angular momentum term and vanishes unless χ_{μ} and χ_{ν} are two different 2p orbitals. These two integrals possess the important property of changing sign when the order of the orbitals is reversed

$$\int \chi_{2s} \nabla_x \psi_{2p_z} d\tau = - \int \chi_{2p_z} \nabla_x \chi_{2s} d\tau = W_{sp}$$

thus with similar expressions for χ_{2p_y} and χ_{2p_x} , and

$$\int \chi_{2p_y} (\mathbf{r} \times \nabla) \chi_{2p_x} d\tau = - \int \chi_{2p_x} (\mathbf{r} \times \nabla) \chi_{2p_y} d\tau = \mathbf{x}$$

$$\int \chi_{2p_x} (\mathbf{r} \times \nabla) \chi_{2p_z} d\tau = - \int \chi_{2p_z} (\mathbf{r} \times \nabla) \chi_{2p_x} d\tau = \mathbf{y}$$

$$\int \chi_{2p_z} (\mathbf{r} \times \nabla) \chi_{2p_y} d\tau = - \int \chi_{2p_y} (\mathbf{r} \times \nabla) \chi_{2p_z} d\tau = \mathbf{z}$$

where \mathbf{x} , \mathbf{y} , and \mathbf{z} are unit vectors in the x , y , and z directions. The molecular orbital expression for the magnetic moment of this transition is therefore

$$\langle \psi_j | m | \psi_i \rangle = -i \sum_A \left[\left\{ (C_{sA_j} C_{xA_i} - C_{xA_j} C_{sA_i}) \mathbf{x} + (C_{sA_i} C_{yA_j} - C_{yA_j} C_{sA_i}) \mathbf{y} + (C_{sA_i} C_{zA_j} - C_{zA_j} C_{sA_i}) \mathbf{z} \right\} \times R_A W_{sp}^A + (C_{yA_j} C_{zA_i} - C_{zA_i} C_{yA_j}) \mathbf{x} + (C_{zA_j} C_{xA_i} - C_{xA_j} C_{zA_i}) \mathbf{y} + (C_{xA_j} C_{yA_i} - C_{yA_j} C_{xA_i}) \mathbf{z} \right] \quad (2.9)$$

(15) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).

The first term corresponds to the magnetic moment resulting from the coupling of all the local electric moments. This is more easily understood if it is remembered that W_{sp}^A is essentially the velocity form of the transition moment integral η_A . The remaining terms of eq 2.9 give the contributions from the local magnetic moments.

Both integrals η_A and W_{sp}^A are readily evaluated from the appropriate Slater orbitals.

Molecular Orbitals of the Cyclohexanones

(A) **Coordinates.** As the exact geometries of cyclohexanone and its derivative are uncertain, the coordinates for these molecules were calculated from idealized models in which all bond angles were assumed tetrahedral, save between the carbon-carbon bonds joining the carbonyl group, for which angle a value of 120° was assumed. The carbon-carbon bonds adjacent to the carbonyl group were assumed to be 1.52 Å, all other carbon-carbon bonds being 1.54 Å. The carbon-hydrogen bonds were assumed to be 1.09 Å and the carbon-oxygen 1.23 Å, and all methyls were assumed to be staggered. The coordinates for cyclohexanone are listed in Table I.

Table I. Coordinates of Cyclohexanone and Methyl-Substituted^a Cyclohexanones

Atom	x	y	z
Cyclohexanone			
C ₁	0	0	0
C ₂	-1.31	-0.76	0
C ₃	-1.25	-1.89	1.05
C ₄	0	-2.71	0.83
C ₅	1.25	-1.89	1.05
C ₆	1.31	-0.76	0
O	0	1.23	0
H ₇	-2.12	-0.07	0.24
H ₈	-1.48	-1.18	-1.0
H ₉	-2.13	-2.53	+0.96
H ₁₀	-1.23	-1.46	+2.05
H ₁₁	0	-3.55	1.61
H ₁₂	0	-3.05	-0.2
H ₁₃	2.13	-2.53	0.96
H ₁₄	1.23	-1.46	2.05
H ₁₅	2.12	-0.07	0.24
H ₁₆	1.48	-1.18	-1.0
H ₇ Substituted			
C ₇	-2.45	0.20	0.35
MH ₁	-2.25	1.09	-0.09
(methyl proton 1)			
MH ₂	-3.40	-0.17	-0.09
MH ₃	-2.55	0.33	1.42
H ₈ Substituted			
C ₈	-1.54	-1.37	-1.38
MH ₁	-0.81	-0.98	-2.10
MH ₂	-2.54	-1.13	-1.74
MH ₃	-1.42	-2.47	-1.33
H ₉ Substituted			
C ₉	-2.44	-2.78	0.93
MH ₁	-3.30	-2.29	1.38
MH ₂	-2.25	-3.72	1.44
MH ₃	-2.66	-2.93	-0.13
H ₁₀ Substituted			
C ₁₀	-1.21	-1.28	2.42
MH ₁	-2.06	-0.61	2.54
MH ₂	-1.26	-2.06	3.20
MH ₃	-0.29	-0.71	2.54

^a Coordinates for methyl group atoms at various H-substitution sites as noted. All methyl groups in *trans* configurations.

(B) **Molecular Orbitals.** As the carbonyl 290 m μ is generally accepted as being an $n \rightarrow \pi^*$ transition, the orbitals ψ_i and ψ_j of eq 2.3 chosen for the calculation were those which were closest to this description. The orbitals chosen for all the molecules studied were the highest occupied molecular orbital, which was found to be a largely oxygen lone-pair orbital, and the first excited orbital, which was almost a pure carbonyl π^* orbital. This choice of orbitals is in good agreement with the 290-m μ system being the first transition in these molecules. These two orbitals for cyclohexanone and all its monomethyl derivatives are listed in Tables II and III. The calculated transition energy corresponds roughly to the transition being at 210 m μ instead of 290 m μ , and this discrepancy is precisely the reason why we prefer to emphasize the rotational strength rather than the rotation.

The first unoccupied orbital, in cyclohexanone, is almost a pure carbonyl antibonding π orbital, with some admixture of hydrogen 1s orbital from H₈ and H₁₆. The main contribution to the highest occupied molecular orbital is from the oxygen 2p_z (lone pair) atomic orbital, but there is also an important *antibonding* contribution from the 2p_z orbital of the adjacent carbon atom, and bonding contributions from the two carbons adjacent to the carbonyl group and some hydrogen 1s character from H₇, H₁₅, H₉, and H₁₃. The nodal surfaces of this orbital are shown in Figure 2. The predicted first transition thus corresponds very closely to the accepted $n \rightarrow \pi^*$ ¹⁴ description of the 290-m μ system of the carbonyl group and there is no difficulty in choosing which orbitals to use in the study of the optical activity of this system.

Because of its diffuse character, the π^* orbital is usually thought of as being more affected by substitution in cyclohexanone than is the lone-pair orbital. The results of the present calculation show (Table IV) that in fact both orbitals are equally perturbed, probably because the "lone-pair" orbital has contributions from nearby carbon atoms and protons, resulting in an orbital which is rather more delocalized than the idealized lone pair (Figures 4 and 5).

Optical Rotatory Strengths

The calculated rotatory strengths (Table IV) are best presented together with a discussion of the octant rule of Moffitt, *et al.*¹⁶ This rule sets out to predict the optical activity induced by substitution in a symmetric cyclic ketone and can be conveniently explained by taking the substituted cyclohexanones as an example. The molecule is divided into octants by the three planes *A*, *B*, and *C* in Figure 1. The first plane, *A*, contains the carbonyl group together with carbon atom 4 and the two protons attached to it, and corresponds to a nodal surface of the n orbital. The second plane, *B*, also contains the carbonyl group together with carbon atoms 2 and 6, and corresponds to one of the two nodal surfaces of the idealized π^* orbital. The remaining plane, *C*, is the second nodal surface of the *idealized* π^* orbital, and assumed by Moffitt, *et al.*,¹⁶ to bisect the carbon-oxygen bond. It should be noted that the position of plane *A* is symmetry determined whereas the positions of the other two planes are estimated from

(16) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

Table II. n Orbitals of Cyclohexanone and Its Monosubstituted Derivatives^{a,b}

Molecule	X ₁	X ₂	X ₈	X ₀	h ₇	h ₁₅	h ₉	h ₁₃
Cyclohexanone	0.35	-0.32	-0.32	-0.61	0.15	-0.15	-0.21	0.21
Stag H ₇	0.36	-0.34	-0.32	-0.58	...	-0.15	-0.20	0.21
Stag H ₈	0.35	-0.34	-0.30	-0.59	0.17	-0.14	-0.20	0.18
Stag H ₉	0.30	-0.29	-0.29	-0.71	0.10	-0.11	...	0.17
Stag H ₁₀	0.34	-0.32	-0.32	-0.61	0.14	-0.15	-0.22	0.21

^a See Figure 1 for notation. ^b Only the largest coefficients are listed. ^c X₁ and X₀ refer to the 2p_z orbitals centered on carbon 1 and oxygen atom, and h₇ refers to the 1s orbital centered on hydrogen H₇.

Table III. π^* Orbitals of Cyclohexanone and Some Monosubstituted Methyl Derivatives^{a,b}

Molecule	Z ₁	Z ₀	h ₈	h ₁₆
Cyclohexanone	0.62	-0.64	0.24	0.24
Stag H ₇	0.62	-0.64	0.25	0.24
Stag H ₈	0.63	-0.63	...	0.26
Stag H ₉	0.60	-0.64	0.25	0.25
Stag H ₁₀	0.62	-0.64	0.23	0.24

^a See Figure 1 for notation. ^b Only the largest coefficients are listed. ^c Z₁ and Z₀ refer to the 2p_z orbital of carbon 1 and the oxygen atom, respectively, h₈ and h₁₆ refer to the 1s orbitals centered on H₈ and H₁₆.

Table IV. Calculated Optical Rotatory Strengths for Cyclohexanone Derivatives

Molecule, proton substituted	$(R \times 10^3 / \mu_e \beta)$	
	Calcd	Obsd
H ₇	+0.00	+ Small (6)
H ₈	+3.51	
H ₉	-2.26	-(5)
H ₁₀	+2.35	
H ₇ , H ₁₃	+3.6	+1.8 (9)
H ₇ , H ₈ , H ₁₃	+5.3	+6.7 (9)

some idealized model for the π^* orbital. The octant rule states that the sign of the optical activity induced by substituting for a proton is given by the sign of the octant in which the proton was situated, and that little or no optical activity is induced by substituting for a proton which lies in either of the three planes, as they are essentially nodal surfaces of the n and π^* orbitals. Before proceeding with the discussion of the calculated rotatory strengths, it is of interest to compare the above description of the nodal surfaces with the findings of the present calculations. As the excited orbital in the predicted first transition corresponds almost exactly to the idealized carbonyl π^* orbital, the calculated nodal plane containing the carbonyl group is, for all practical purposes, coincident with *B*. The calculated point of intersection of the second nodal surface, *C*, with the carbon-oxygen bond is also in good agreement with the original guess of Moffitt, *et al.*,¹⁶ being 0.6 Å from the carbon. The position of plane *A* is symmetry determined and is the plane marked A-A in Figure 2. As the n orbital differs significantly from the idealized lone-pair orbital in having an antibonding contribution from the adjacent carbon atom, there is an extra nodal surface in the region of the carbonyl group, *C'* in Figure 2. This extra surface should, in principle, be considered in the formulation of the octant rule, however it need not be included explicitly as it is almost coincident with *C* in the region of the carbonyl group.

As the equatorial proton of carbon atom 2 lies in a positive octant, and almost in the plane *B*, the octant rule predicts a small positive rotation for H₇ in methylcyclohexanone. The calculated rotatory strength was found to be almost zero, in good agreement with this

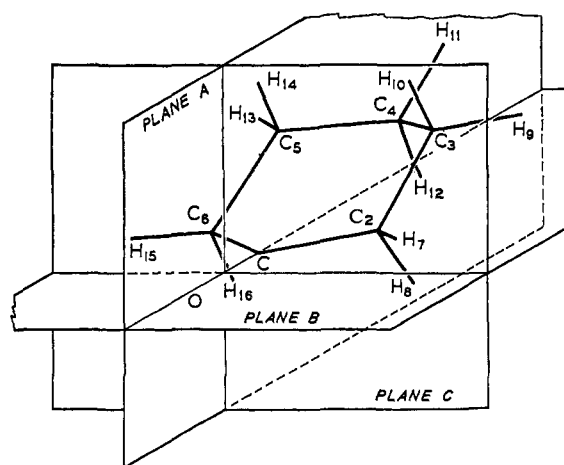
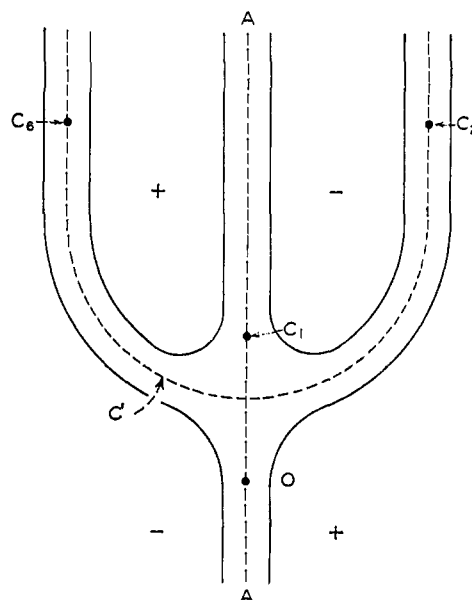


Figure 1. Cyclohexane: numbering convention and location of nodal planes.

Figure 2. Nodal surfaces of the n orbital in cyclohexanone. Surface *C'* is due to nonlocalized nature of the n orbital.

prediction. It is important to realize that the substituent must have a plane of symmetry which is coincident with *B* in the substituted molecule for this low rotational strength to result. This condition is satisfied by the methyl group in the staggered configuration as

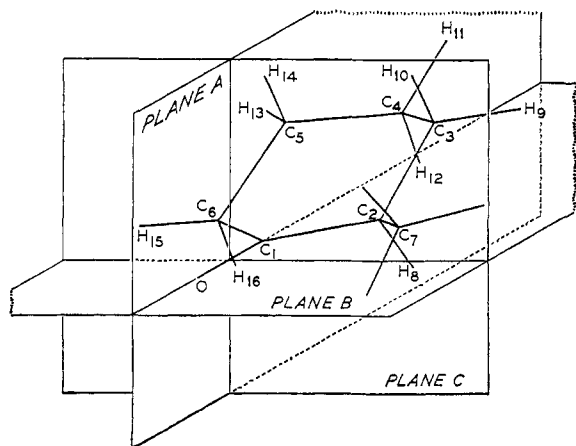


Figure 3. Methyl substituent group in cyclohexanone. Group is shown in "staggered" position.

one proton is then almost in the plane *B* with the remaining protons symmetrically situated on either side. In fact, if this situation is disturbed, large rotational strengths can result; for example, 2.38 was calculated for the asymmetric configuration shown in Figure 3. The second proton of atom 2 is also in the positive octant, but is well removed from *B*, and hence its substitution is expected to lead to a positive rotatory strength; the calculated value of 3.5 is in good agreement with this. As both protons of atom 3 are in negative octants and well separated from any nodal planes, negative rotational strengths are predicted by the octant rule for both H_9 and H_{10} of methylcyclohexanone. The calculated value for substitution at the equatorial proton is -2.26 , and there is some direct experimental evidence, in that the rotation¹⁷ of (+)-3-methylcyclohexanone is observed to be positive, in support of this result. However, the sign of the rotatory strength ($+2.4$) calculated for substitution of the axial proton (H_{10}) is opposite to that predicted by the octant rule. There are, however, no measurements on this molecule at the present time, and further calculations on related decalone molecules are necessary before any conclusion can be drawn.

Rotatory strengths have also been calculated for 2,5-dimethylcyclohexanone and 2,2,5-trimethylcyclohexanone, for comparison with the values obtained by Moscowitz.⁷ The calculated rotatory strengths (Table IV) are of the same order of magnitude and are in substantial agreement with the measured results.

Unfortunately, because of the inherent complexity of the SCF method, it is difficult to isolate those interactions between the methyl and carbonyl groups which are responsible for the optical activity, although it seems likely that indirect interactions involving one or more intervening groups are important. Similarly it is difficult to relate changes in the n and π^* orbitals resulting from methyl substitution in cyclohexanone to the orbitals of the unsubstituted molecule, although part of the induced electric transition moment can be ascribed to the admixture of some π character (bonding between the carbon and oxygen atoms of the carbonyl group) into the carbonyl n orbital.

(17) C. Djerassi and G. W. Krakower, *J. Am. Chem. Soc.*, **81**, 237 (1959).

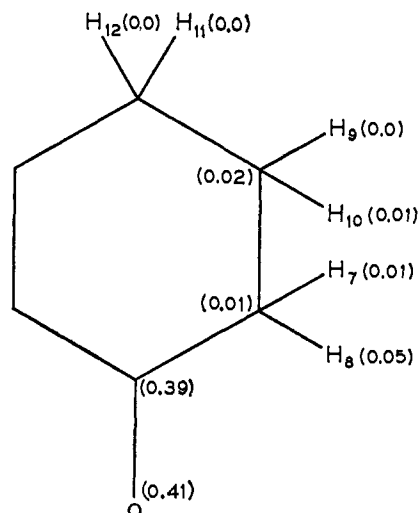


Figure 4. Electron distribution of the n orbital of cyclohexanone. The value at the carbon and oxygen atoms was calculated from the sum of the squares of the $2s$, $2p_x$, $2p_y$, and $2p_z$ coefficients in the n orbital; the proton values are simply given by the square of the appropriate $1s$ coefficients in the n orbital. In the case of the carbon and oxygen atoms the dominant contribution is from the $2p_x$ orbital.

The simple theory developed above permits the rotatory strength to be analyzed in terms of atomic contributions which then give an indication of the nature of the induced optical activity and the region of the molecule from which it originates. The magnetic transition moments of all molecule studies were virtually unchanged from the cyclohexanone value of 0.5β along the C-O band, and arose from local atomic circulations on both the carbon and oxygen of the carbonyl group. The constancy of the magnetic transition moment indicates that the variations in the optical activity observed between these molecules are to be associated with variations in the electric transition moment. The calculated electric moment was found not to depend on the near cancellation of a large number of terms, but rather, to be determined by the contributions from three centers. The most important contribution, which generally determines the sign of the rotatory strength, is the moment induced in the carbonyl group. This result confirms the assumption made by Moscowitz in his theory of rotatory strengths.⁷ There are, however, further contributions from the remainder of the molecule, of which only the contributions from the carbon of the methyl group and the proton, left "unpaired" by substitution, are significant. As might be expected these last two contributions tend to be of opposite sign. These results encourage the hope that the present molecular orbital theory can make definite predictions concerning the magnitude and sign of rotatory strengths.

Summary and Conclusions

A simple, one-center, LCAO MO theory of optical rotatory strengths has been developed, and used in conjunction with approximate SCF MO to study the optical activity of the 290- μ system of the carbonyl chromophore in the cyclohexanones. The highest occupied and first excited molecular orbital correspond very closely to an oxygen lone pair and carbonyl antibonding π orbital, respectively (Figures 4 and 5). The

highest occupied orbital differed from the idealized oxygen lone-pair orbital in having a significant anti-bonding contribution from the adjacent carbon atom. Thus the predicted first transition corresponded very closely to the expected $n \rightarrow \pi^*$. The position of the π^* nodal plane which is perpendicular to the carbonyl group, plane *C* of Figure 3, was calculated and found to almost bisect the carbon-oxygen bond. Also, as the n orbital is slightly antibonding between the carbon and the oxygen there is a further nodal surface in this region. In practice, this surface is of little importance as it is almost coincident with *C* in the region of the carbonyl group.

The calculated rotatory strengths agree well with the observed values in all but one case. A breakdown of the calculated rotatory strength into atomic contributions showed the magnetic moment to be sensibly constant in the series of molecules studied, and to be almost unchanged from the transition magnetic moment of the $n \rightarrow \pi^*$ system in cyclohexanone. The transition electric moment is mainly induced in the carbonyl group, but there are important contributions from other groups in the molecule. The calculated rotatory strengths were also found to be very dependent upon the configuration of the methyl group.

In the present calculation, the character of the optically active transition was well understood from spectral studies, and the calculation mainly served to confirm the assignment and to illustrate the nature of the optical activity in these molecules. However, the success of this calculation encourages hope that the

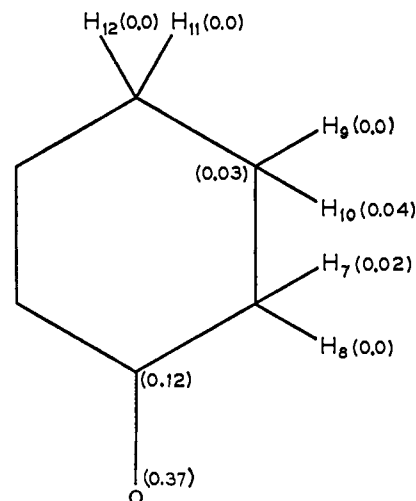


Figure 5. Electron distribution in the π^* orbital of cyclohexanone (see note on Figure 4 for the method of calculation). In the case of the carbonyl atoms the dominant contribution is from the $2p_z$ orbitals, although in the case of the carbon there is a very small amount of $2s$ character.

theory may prove useful in the interpretation of the optical activity of less well understood transitions in other chromophores.

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Organic Reactions under High Pressure. X. The Mechanism of Aldehyde Polymerization at High Pressures¹

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Abstract: The polymerization of *n*-butyraldehyde at 6000–8000 atm and 25° responds to none of the usual tests for a radical chain process. It is neither initiated by di-*t*-butyl peroxyoxalate nor inhibited by galvinoxyl and shows no evidence for copolymerization with methyl methacrylate or diethyl fumarate. Traces of carboxylic acids, however, catalyze the reaction indicating that propagation involves simple acid-catalyzed hemiacetal formation. Contrary results in the literature are ascribed to depolymerization before samples were examined or irreversible conversion to parabutryraldehyde. A striking catalysis is observed by hindered phenols, notably tri-*t*-butylphenol, which also catalyzes polymerization at –100° and atmospheric pressure. Polybutyraldehyde may be stabilized by end-group acetylation by ketene or by carrying out the pressure polymerization in the presence of acetic anhydride.

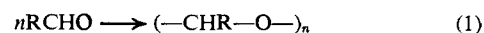
In 1929 Bridgman and Conant³ reported that *n*-butyraldehyde and isobutyraldehyde, subjected to a pressure of 12,000 atm for 40 hr, were converted to waxy solids which slowly reverted to aldehyde on standing at atmospheric pressure. Further study by

(1) Taken from the Ph.D. Dissertation of T. A. Augurt, Columbia University, 1965. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) DuPont Teaching Fellow, 1962–1963; Trubeck Fellow, 1963–1964.

(3) P. W. Bridgman and J. B. Conant, *Proc. Natl. Acad. Sci. U. S.*, **15**, 680 (1929).

Conant^{4,5} indicated that the polymer had the structure of polyacetal



with the nature of the end groups undetermined, and that the rate of polymerization depended markedly on aldehyde purity. Thus, freshly distilled aldehyde gave little or no polymer, while samples exposed to ozone or

(4) J. B. Conant and G. O. Tongberg, *J. Am. Chem. Soc.*, **52**, 1669 (1930).

(5) J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932).