Table III. The Net Atomic Charges (× 10^{-3} e)[a]

Compd	Y_a	O_1	O_2	O_3	O_4	Y_b
H_2O	−169.12	−338.25				−169.12
F_2O	−17.90	35.81				−17.90
H_2O_2	190.87	−190.87	−190.87			190.87
F_2O_2	−16.81	16.81	16.81			−16.81
H_2O_3	204.72	−167.58	−50.25	−191.14		204.25
F_2O_3	−12.20	28.47	−14.81	3.58		−5.03
H_2O_4	290.95	−178.30	−31.64	−31.64	−178.30	290.95
F_2O_4	−3.02	7.39	−4.35	−4.35	7.39	−3.02
$(CH_3)_2O$	(C) −78.89	−232.44				(C) −74.40
$(CF_3)_2O$	(C) 544.79	−257.84				(C) 546.84
$(CH_3)_2O_2$	(C) −80.01	−137.45	−141.20			(C) −84.64
$(CF_3)_2O_2$	(C) 546.37	−134.59	−140.02			(C) 543.98
$(CH_3)_2O_3$	(C) −81.10	−122.54	−61.53	−143.07		(C) −80.51
$(CF_3)_2O_3$	(C) 547.29	−122.23	−42.66	−146.28		(C) 549.17

[a] The term net atomic charge is defined as $Z - n$(STO-4G), where Z is the atomic number, and n is the net electron density of an atom.

As in the case of hydrogen trioxides, the calculations show a slight preference of the decomposition to the corresponding fluorine oxide or dialkyl ether, respectively. An apparent calculated greater stability of alkyl trioxide compared to fluorine substituted compound (Y = CF_3) is not in accord with experimental observations. This may be due to the fact that the decomposition path cannot be followed; the initial and the final state were considered only.

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The Octant Rule. 5. On the Nature of the Third Nodal Surface. An Understanding of "Anti-Octant" and Front Octant Effects by a CNDO/S Study of Rotatory Strengths of the Carbonyl n → π* Transition[1]

Thomas D. Bouman*[2a,b] and David A. Lightner[2c]

Contribution from the Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and University of Nevada, Reno, Nevada 89507.

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Abstract: The Del Bene–Jaffé parameterization of the CNDO SCF-LCAO-MO method is shown to reproduce well the rotatory strengths of the n → π* transition in ketones without the use of configuration interaction. Rotatory strengths for a series of methylcyclohexanones and *cis*- and *trans*-decalones are calculated, and computational support for the "primary zigzag" hypothesis of Kirk and Klyne is provided. The nature of the third surface, dividing front and back octants, is explored with a series of flexible model compounds in which a single dissymmetric methyl group is moved through space, and the signed rotatory strength computed as a function of position. The computed regions of sign change account for many of the supposed "anti-octant" effects observed.

For more than 15 years, the octant rule of Moffitt et al.[3] has been the subject of considerable interest by both experimentalists and theorists. In its simplest form, the rule states that the space surrounding the carbonyl chromophore in an optically active ketone is divided into eight regions by (i) the two symmetry planes of the isolated (C_{2v}) chromophore, and (ii) by a third plane perpendicular to and bisecting the C=O bond. If these three planes are taken to define a Cartesian coordinate system, then the *sign* of the contribution made by an alkyl substituent to the observed circular dichroism (CD) of the n → π* transition varies as the *sign* of the product $X \cdot Y \cdot Z$ of the atomic coordinates. Atoms having counterparts symmetrically placed across the carbonyl symmetry planes will exert no effect on the CD, due to cancelation. This geometrical rule, so simple and straightforward to apply, has served to assist in establishing the absolute configurations of a large number of compounds.[4] The octant rule has also spawned numerous attempts at establishing sector rules appropriate both to different substituents in ketones, and to different chromophores, with varying degrees of success.[5,6] Halogen atom substituents, for example, are known to obey the octant rule in the same sense as a methyl group, save for the well-known anomalous behavior of fluorine.[7,8] The proper role of other polar substituents, such as carboxyl or hydroxyl, is less clear.

Quite early, however, Moffitt et al.[3] recognized several potential problems in applying the octant rule. These include, inter alia, the (then) uncertain assignment of hydrogen atom contributions and the effects of unforeseen distortions from the "idealized" geometries employed in applying the rule. Perhaps the most widely discussed reservation originally expressed addresses the existence and shape of the "third surface". As Schellman[9] has shown, a quadrant rule is the minimum sector rule for the carbonyl chromophore, and the quadrants are defined by the intersecting (local) symmetry planes. Further subdivision into octants depends on the nature and nodal properties of the wave functions associated with the n → π* transition. The applicability of any sector rule depends on the extent to which the chromophore in question retains its identity in the molecule as a whole, i.e., the extent to which the remainder of the molecule can be considered as a perturbation in determining the chiroptical properties of the chromophoric electronic transition. These conditions have been recently reviewed by Deutsche et al.[5]

Because of the paucity of unambiguous "front-octant" experimental data, and the demonstrated dependence of sector-rule behavior on an assumed computational model,[8,10] theoretical studies have been free to embrace either a quadrant[9,11] or an octant[8,12-14] rule. Recently, however, compounds have been prepared in which dissymmetrically placed substituents are unequivocally located in what would be front octant regions,[1,15] and the observed CD supports the octant rather than the quadrant rule.

Moffitt et al.[3] took the third surface to be a plane bisecting the C=O bond purely for convenience rather than on any theoretical ground. Indeed, they specifically cautioned that this surface was very probably *not* a plane. Intimations that the surface might be curved came initially from calculations by Pao and Santry,[16] who predicted an "anti-octant" behavior for 3(a)-methylcyclohexanone, a conclusion subsequently confirmed by Snatzke's synthesis of and CD data on the corresponding conformationally rigid β-substituted methyladamantanones.[17] The same type of behavior has been observed by Lightner and Jackman[18] in *exo*-2-methylbicyclo-[2.2.1]heptan-7-one. Pao and Santry suggested that the third surface envelops the unsubstituted molecule, and that substituents may penetrate it. Coulombeau and Rassat[19] have analyzed CD and ORD data for a number of compounds, and have made the interesting proposal of a surface rather sharply curved *away* from the carbonyl oxygen. Thus, alleged "anti-octant" behavior would be explained by the substituent actually lying in *front* of the third surface as newly defined. Tocanne[20] draws a similar conclusion from his cyclopropyl ketone work, whereas Allinger and Riew[21] conclude that the original octant rule is invalid, even despite its recognized[3] difficulties (vide ante).

Kirk and Klyne,[22] on the other hand, have proposed a somewhat different model for observed CD signs and magnitudes, based on a very extensive analysis of decalones and their extended analogues. These authors have adopted the view of Hudec and co-workers[23] (cf. also Howell[12]), that interactions within the hydrocarbon chains outside the chromophore, rather than direct perturbative action on the carbonyl group itself, dominate the contributions to the induced rotatory power. Further, they assert that the "through-bond" interactions are quite sensitive to chain conformations, reaching appreciable values only when a planar zigzag (W shaped) path can be traced along the bonds from the carbonyl group to the dissymmetrically placed substituent. Within this framework, Kirk and Klyne have been able to integrate the data for both *cis*- and *trans*-decalones, as well as the "anti-octant" compounds of Snatzke,[17] into a single empirical scheme. The shape of a third surface in this analysis, however, is more difficult to assess.

In the present study, we have undertaken to characterize the "third surface", and to analyze the "primary zigzag" hypothesis of Kirk and Klyne[22] and Hudec.[23] We will first describe a computational model for chiroptical properties of the n → π* transition; then we will apply it to a number of compounds for which CD data are available; finally we will examine a series of conformationally flexible model compounds as a function of torsional angles, by which the variation of rotatory strength with position of a methyl group will be explored. The data allow us to describe the shape of the third nodal surface and the sign-determining regions of the octant rule.

Method

The rotatory strength of the transition 0 → i is defined quantum mechanically[14] as

$$R'_{0i} = \mathrm{Im}\,\{\langle\Psi_0|\mu|\Psi_i\rangle\cdot\langle\Psi_i|\mathbf{m}|\Psi_0\rangle\}$$

where Ψ_0 and Ψ_i are respectively the ground and excited state wave functions, μ and $\mathbf{m}$ are respectively the electric and magnetic dipole moment operators, and $\mathrm{Im}(a + ib) = b$. The magnetic dipole moment operator is $\mathbf{m} = -(ie\hbar/2mc)\Sigma_\nu \mathbf{r}_\nu \times \nabla_\nu$. The electric moment can be evaluated using length, velocity, or acceleration operators, owing to the operator equations connecting them for exact wave functions.[24] For approximate wave functions, the relations are not exact, and one therefore has to choose an operator on grounds of convenience, results, or other apposite criteria. We have used the velocity form, in which

$$\langle\psi_1|\mu|\psi_2\rangle = \frac{e\hbar^2}{m}\left\langle \psi_1\middle| \sum_\nu \nabla_\nu \middle|\psi_2\right\rangle/(E_2 - E_1)$$

in order that the rotatory strengths be origin independent for approximate wave functions.[25] It has become customary to express results in terms of the reduced rotatory strength, R_{0i}, defined as 100 $R'_{0i}/D\beta$,[14] where D is the Debye unit, and $\beta = |e|\,\hbar/2mc$ is the Bohr magneton. If atomic units are used for the operators, and the transition energy is expressed in electron volts, one obtains

$$R_{0i} = 6916\,\{\langle\Psi_0|\nabla|\Psi_i\rangle\cdot\langle\Psi_0|\mathbf{r}\times\nabla|\Psi_i\rangle\}/\Delta E_{0i}$$

Since both ∇ and $\mathbf{r} \times \nabla$ are one-electron operators, their matrix elements over any suitable basis are not difficult to evaluate. The latter reduce, in a Slater basis, to combinations of overlap integrals, and their formulas have been given elsewhere.[26,27] The ∇ integrals in a Slater basis are evaluated with the C function method of Fraga,[28] using formulas derived for real wave functions by Richardson.[26] Given a suitable wave function expressible as a linear combination of determinantal MO configurations built up from linear combinations of Slater-type atomic orbitals (AO's), the rotatory strength may be easily evaluated. We have used Richardson's Fortran program ROTSTR,[29] which incorporates these algorithms, and which we have modified for the present study.

The stumbling block in the calculation, as always, is the determination of sufficiently good wave functions Ψ. Although ab initio calculations at the STO-3G level are becoming available for molecules the size of methylcyclohexanone,[30] one

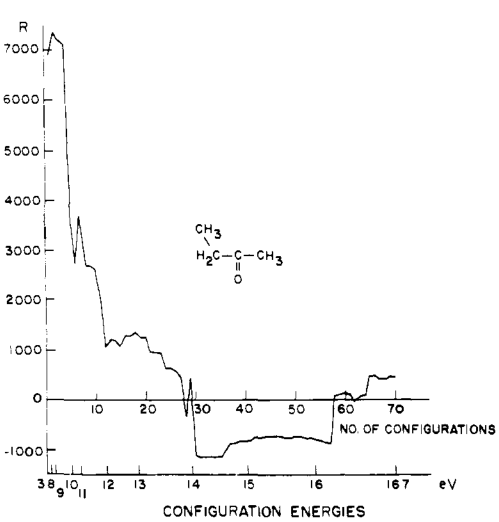

Figure 1. Rotatory strength (arbitrary units) of methyl ethyl ketone in conformation V vs. number of singly excited configurations included in the CNDO/S-CI calculation. Energies of the configurations are indicated on the lower scale.

must still resort to more approximate, semiempirical calculations for comparative studies of many of the large molecules one encounters in applications of the octant rule.

We have chosen to use the CNDO/S method of Del Bene and Jaffé,[31] in which the parameters of the approximate SCF-LCAO-MO scheme are chosen to reproduce spectroscopic properties of low-lying electronic transitions in organic molecules, rather than accurate ground state energies. It has been applied successfully to describing n → π* transitions in nitrogen-containing aromatic compounds, among others.[31] All valence electrons (1s on H, 2s, 2p on first-row elements) are included. The method has the virtue common to zero-differential-overlap (ZDO) approaches of being fast enough to apply to molecules containing ten or more heavy atoms, while the parameterization is such as to reproduce the observed n → π* transition energy in aliphatic ketones to within 0.2 eV. As with any other approximate method, its reliability must be established by comparison with experimental data. We believe this should be done anew for each chromophore studied, particularly for sensitive properties such as rotatory strengths; the method can then be used as an extrapolation scheme to make predictions for related compounds.

The CNDO/S parameters reproduce the 270-300-nm excitation wavelength of the carbonyl n → π* transition acceptably well for all compounds considered, if only the single configuration defining the transition is used to represent the excited state wave function (properly antisymmetrized for spin). Del Bene and Jaffé[31] advocate the use of limited configuration interaction (CI) to "improve" the description of the excited state; however, the n → π* *configuration* so dominates ($c \gtrsim 0.95$) a limited CI description of the excited state in aliphatic ketones that little change in the charge distribution results from keeping only the first term. Indeed, if other singly excited configurations are allowed to mix variationally with the n → π* term, the transition is strongly shifted to lower energies.

The effects of CI on the chiroptical properties of the transition are even more profound. The carbonyl chromophore is classed as inherently symmetric,[32] with local C_{2v} symmetry; as such, the electric dipole transition moment for the lowest transition is zero to first approximation (neglecting vibronic interactions). Thus electric-dipole-allowed transitions included in the CI description may make a disproportionate contribution to the overall transition moment, even though their variationally determined mixing coefficients are small ($c \lesssim 0.2$). Figure 1 shows the variation of rotatory strength with the number of lowest singly excited configurations included in the CI description for one conformation of methyl ethyl ketone. The rotatory strength shows no sign of converging even after 70 configurations, and the presence of several sign changes and plateaus in the curve serves to dispel whatever confidence might remain in any limited CI calculation in this context.

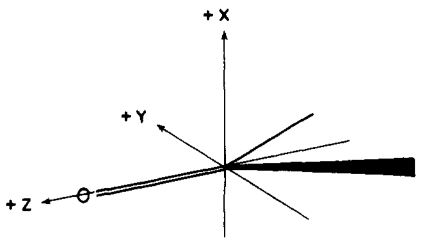

Figure 2. Cartesian coordinate system used for all calculations.

Michl et al.[33] have studied the convergence of CI expansions in determining intensities and polarization directions (both of which are determined by electric dipole transition moment integrals) for various transitions of planar molecules in a Pariser-Parr-Pople framework. These authors begin with a CI basis including *all* singly excited configurations arising from the π-electron MO's, and then add selected doubly and triply excited configurations until convergence is obtained. They use a numerical criterion for inclusion of a configuration based on the magnitude of the product of the CI coefficient and the transition matrix element, since a substantial contribution can be made to weak transitions if either the CI coefficient or the integral is large. Both dipole length and dipole velocity forms of the transition moment integrals were used and compared. The results show that CI expansions lead to very slowly convergent optical properties for weak transitions; moreover, the size of the resulting CI basis restricts such a calculation to systems with a small number of electrons.

In the compounds we are considering, the magnetic moment of the n → π* transition is large, calculated to be about 1 μ_B, and strongly polarized in the Z direction (see Figure 2).[34] As a result, the rotatory strength is essentially (about 93%) determined by the Z component of the scalar product, and hence by the quantity $\langle \Psi_0 | \nabla_z | \Psi_i \rangle$. We attempted to assess the effect of including additional configurations in the basis by doing a calculation of R for a chiral conformation of acetaldehyde.[12] The 63 singly excited configurations arising in the minimum valence-shell basis showed the same erratic contributions to R as in the previous calculation. In accord with the assessments of Huzinaga and Arnau[35] and Morokuma and Iwata,[36] the single excitations making significant contributions to the transition moment are found to be those either out of the *n* orbital or into the π* orbital. One expects that the doubly excited configurations most effective in improving the ground state for this transition are pairwise excitations involving the same orbitals as above. When these are included, using a general CNDO-CI program provided by D. D. Shillady,[37] one finds that although their mixing coefficients are appreciable, they make essentially no contribution to the transition moment. Due to limitations of computer memory and running time, it was not practicable to add further configurations.

Richardson et al.[26] and Imamura et al.[38] have argued that, since the AO's in a zero-differential overlap (ZDO) scheme may be considered as Slater-type orbitals which have been subjected to an orthogonalization transformation, the calculated MO's should be "deorthogonalized" before two-center atomic matrix elements of ∇ and $\mathbf{r} \times \nabla$ are evaluated over them. However, changes in the calculated rotatory strengths induced by this procedure are small for the carbonyl systems examined here, and in our opinion represent an elaboration unwarranted by the sophistication of the method. Furthermore, Hansen's[39] analysis of corrections to electric dipole transition moment integrals over orthogonal and nonorthogonal bases shows that the corrections to two-center terms are minimized if the dipole velocity form is used. Corrections to non-nearest neighbor terms, and first-order overlap corrections to the magnetic moment integrals, arising from the orthogonalization transformation, have not been included here, for the reason stated above. In our calculations all integrals of ∇ and $\mathbf{r} \times \nabla$ have been retained, as evaluated over the Slater-orbital basis.

We conclude that, for the purpose of obtaining a single, simple model for comparisons of optical activity among a wide variety of saturated ketones, the method as we have described it is adequate. It should be emphasized, however, that different chromophores and/or different (nonalkyl) substituents may require different parameterizations or more elaborate models.

Calculations

In all the subsequent calculations, we use the system of coordinate axes shown in Figure 2. The Z axis lies along the C=O bond, and the carbonyl group lies in the Y-Z plane. Thus the X direction is the "π" direction, and the "nonbonding" orbital lies largely in the Y-Z plane.

The atomic Cartesian coordinates for all chair cyclohexanone derivatives and the straight-chain model ketones we describe later were derived from the idealized cyclohexane geometry, with all bond angles tetrahedral, $R_{\mathrm{C-O}} = 1.22$ Å, $R_{\mathrm{C-C}} = 1.54$ Å, and $R_{\mathrm{C-H}} = 1.09$ Å. As pointed out in the original octant rule paper,[3] the true cyclohexanone geometry appears to be only very slightly distorted from the ideal, with a carbonyl C-C-C bond angle of about 116°, and carbonyl C-C_2 bond lengths of 1.51 Å. Calculated rotatory strengths vary by up to several units as the geometry is changed within these limits, but this is deemed to be well within both the uncertainty in the theoretical method and the variability in reported $\Delta\epsilon$ values induced by solvent effects, difficulties in assessing optical purity, and inherent experimental uncertainties.

Coordinates for the model ketones in which torsional angles were varied were calculated from the idealized geometry, ex-

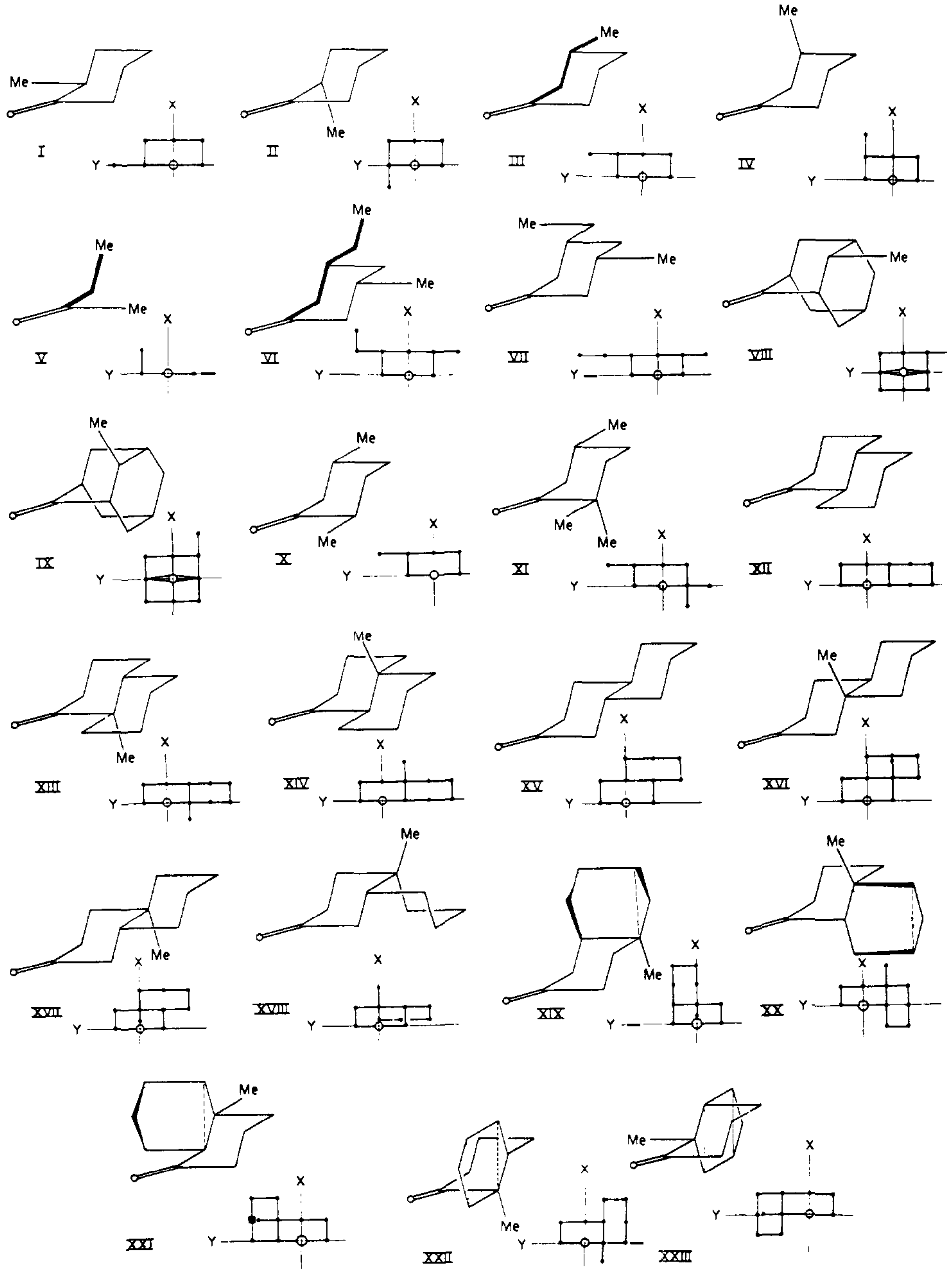

Figure 3. Perspective drawings and octant projections of compounds and conformations comprising Table I. In compounds III, V, and VI the "primary zigzag" of Kirk and Klyne is indicated by heavy lines. All six-membered rings are in the chair form.

Table I. Comparison of Calculated and Observed Chiroptical Properties for Compounds Derived from Chair Cyclohexanones

	Calcd		Obsd	
Compd	R	λ_{max}	$\Delta\epsilon$	Notes
2(e)-Methylcyclohexanone (I)	−4.7	293	(+0.2)	*c, d*
2(a)-Methylcyclohexanone (II)	−10.2	297	−0.3, (−1.2)[c,d]	*a, b, f*
3(e)-Methylcyclohexanone (III)	+16.7	290	+0.5	*d*
3(a)-Methylcyclohexanone (IV)	−7.0	294	(−0.1)	*c, d*
Methyl ethyl ketone ($\phi = 120°$) (V)	+18.8	315	(+1.6 ± 0.2)	*c, d*
3(e)-Ethyl-5(e)-methylcyclohexanone (VI)	+12.5	280	(+0.6 ± 0.2)	*c, d*
3(e)-Ethyl-5(e)-methylcyclohexanone (VII)	−0.6	277	(−0.25)	*c, d*
(−)β(e)-Methyladamantanone (VIII)	−10.4	283	−0.57 to −0.87	*b, g*
β(a)-Methyladamantanone (IX)	+5.3	288	+0.09 to −0.05	*g*
2,5-Dimethylcyclohexanone (X)	+18.6	289	+0.65	*a, f*
2,2,5-Trimethylcyclohexanone (XI)	+25.8	292	+2.0	*a, f*
trans-1-Decalone (XII)	−7.2	262	−0.81 to −0.95	*b, d*
9-Methyl-*trans*-1-decalone (XIII)	−1.9	268	+0.7	*a, d*
10-Methyl-*trans*-1-decalone (XIV)	−1.6	261	−0.4	*a, d*
trans-2-Decalone (XV)	−49.0	264	−1.12 to −1.37	*d*
9-Methyl-*trans*-2-decalone (XVI)	−41.2	263	(−1.55 to −2.0)	*b, e*
10-Methyl-*trans*-2-decalone (XVII)	−50.4	263	−0.64, −1.2[a]	*b, d*
10-Methyl-*cis*-2-decalone (XVIII)	−29.0	273	(−0.5)	*d, e*
10-Methyl-*cis*-2-decalone (XIX)	−9.7	291	(−0.1)	*d, e*
30:70 mixture of XVIII and XIX	−15.5		−0.3	*d*
10-Methyl-*cis*-1-decalone (XX)	+15.8	277	(+2.1) +0.3	*d, e*
10-Methyl-*cis*-1-decalone (XXI)	−35.0	278	(+0.2)	
9-Methyl-*cis*-1-decalone (XXII)	+49.1	291	(+2.1) +1.3[a]	*d, e*
9-Methyl-*cis*-1-decalone (XXIII)	−6.2	279	(−1.85)	

[a] Calculated from ORD amplitude by $\Delta\epsilon = a/40.3$. [b] Experiment performed on enantiomer; sign of $\Delta\epsilon$ changed. [c] Calculated average of $\Delta\Delta\epsilon$ values for other compounds. [d] D. N. Kirk and W. Klyne, *J. Chem. Soc., Perkin Trans. 1*, 1076 (1974). [e] Values in parentheses predicted by Kirk and Klyne. [f] C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963). [g] G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968); G. Snatzke, B. Ehrig, and H. Klein, *ibid.*, **25**, 5601 (1969).

pressed in terms of bond lengths, bond angles, and dihedral angles, by the computer program CART,[40] provided to us by Dr. C.-Y. Yeh.

Our programs were run on the Control Data 6400 at the University of Virginia. Running times ranged from 2–6.5 min for the cyclohexanone derivatives, and 0.5–3 min for the flexible model compounds, depending on the number of orbitals. About 85–90% of the time was used in calculating the CNDO/S wave functions. The CNDO/S program[31] was modified to interface directly with the ROTSTR program.[29]

General Features of the Results. The "nonbonding" (n) orbital, often described as a lone pair on the carbonyl oxygen, is found to be alternatively antibonding and bonding along the chain O–C–C_α–C_β–C_γ in the molecules we have studied. Orbital electron densities fall generally around 0.35–0.40 on the oxygen, 0.14–0.17 on the carbonyl carbon, and 0.13–0.16 on each α carbon. Thus only about 50% of the electron is on the C═O group itself, whereas including the α carbons in the chromophore accounts for roughly 85% of the electron density. The remainder of the orbital is delocalized over the whole molecule. Changes in structure affect primarily the electron density on oxygen, in the n orbital, while the three carbon atoms in the chromophore remain virtually unchanged. The π^* orbital, on the other hand, is calculated to be almost completely localized on the C═O group, accounting for about 94% of the electron density. The only other contributions of any size (MO coefficients around 0.1) come from the α-axial positions. The orbital changes very little from molecule to molecule. It is reassuring in any case to be able to ascribe changes in the rotatory strength primarily to the n orbital, since structural inferences drawn from the optical activity are assumed to be ground state properties.

Orbital energies for the n orbital in this model cluster around −10.5 eV, within about 0.1 eV, while those for the π^* orbital are grouped about +0.4 eV. The n orbital energy is separated by at least 1–2 eV from other occupied orbitals, and the π^* energy is at least 2–3 eV lower than the other virtual orbitals. The latter are generally closely spaced in energy. Departures of more than 0.2 eV from these energies usually signalled severe steric crowding in the conformation chosen.

Derivatives of Chair Cyclohexanone and Calibration of the Method. To establish the degree of reliability of the CNDO/S method for computing rotatory strengths for ketones, we have performed computations on a number of substituted cyclohexanones and decalones.[3,19,22] We have included many of the molecules on which the octant rule was originally based.[3] Figure 3 shows perspective drawings and octant projections (as viewed from $Z = +\infty$) for each molecule, in the absolute configuration chosen. The comparison of calculated rotatory strengths with observed $\Delta\epsilon$ values is presented in Table I. It will be seen that the qualitative agreement in sign and magnitude is generally good, with exceptional cases to be discussed separately. The calculated R values are uniformly larger than would be obtained by integration of the experimental CD curve; however, a rough scale factor of $\Delta\epsilon = 1$ corresponding to $R = 25$, within a factor of 2, will serve to assist in correlating calculated and experimental properties. One may, at any rate, make qualitative predictions of magnitude that agree well with experiment.

The results for the four methylcyclohexanones agree in sign and relative magnitude with such experimental data as are available. These compounds have been favorite subjects of earlier calculations;[16,30,41–43] all of them except Tai and Allinger's[41] predict the "anti-octant" behavior of the 3-axial methyl group (IV), as do we. We find that the 3-equatorial substitution (III) gives a larger rotatory strength than the 2-axial (II), in agreement with Gould and Hoffmann,[42] but contrary to Pao and Santry.[16] The available experiments also indicate this effect, contrary to the results of Moffitt et al.,[3] based on ORD curves. We agree with Gould and Hoffmann[42]

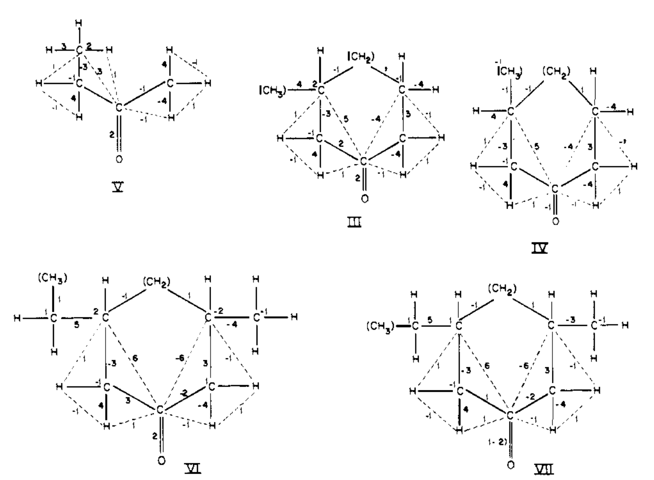

Figure 4. Principal contributions (×10^3) to $\langle n|\nabla_z|\pi^*\rangle$ in atomic units, for compounds indicated. For clarity, only those terms with magnitude one or greater, to one significant figure, are shown. Atom groups are enclosed in parentheses to avoid confusion of subscripts with matrix element terms. Nonbonded terms are indicated by broken lines.

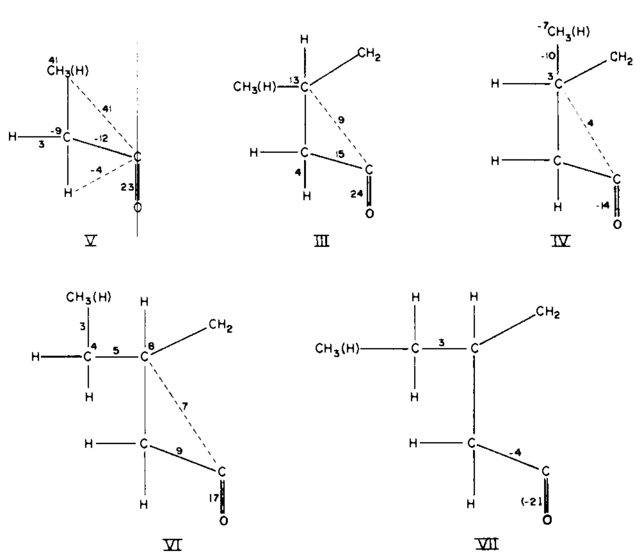

Figure 5. Principal contributions (×10^4) to $\langle n|\nabla_z|\pi^*\rangle$ in atomic units, after cancelation across the X–Z plane. The H atom balancing the methyl group on the $-Y$ side is indicated in parentheses. Only those terms greater than 2 × 10^{-4} au are shown, for clarity.

in assigning a relatively weak *negative* CD to the 2-equatorial position (I), while Tai and Allinger[41] predict a weakly *positive* amplitude. That is, we find that the methyl group acts as if it were in the lower left back octant rather than in the carbonyl plane. Of course that plane is no longer a symmetry plane in chair cyclohexanone, and therefore the rotatory strength due to an α-equatorial substituent need not be strictly zero. Kirk and Klyne[22] assign a weakly *positive* CD increment to this position, based on $\delta\Delta\epsilon$ values. Computations of CD amplitudes near zero will be most subject to any inadequacies in the model; the same can be said as well for the experimental results, as witness the sign change observed by Snatzke[17] in the 3-substituted adamananone as a function of solvent. Both Tai and Allinger[41] and Imamura et al.[43] predict that the 3-axial methyl should exert nearly three times as great an effect as the 3-equatorial, contrary to our results and to experiment.

We have analyzed the $\langle n|\nabla_z|\pi^*\rangle$ matrix element, which is essentially responsible for the rotatory strength, into one- and two-center atomic contributions by weighting the AO matrix elements with the products of their MO coefficients in the n and π^* orbitals, and summing over all orbitals on an atom. The results are displayed in Figure 4, along with those for three flexible compounds in conformations that either extend Kirk and Klyne's primary zigzag,[22] or destroy it. Methyl ethyl ketone in a conformation twisted 120° from the planar extended form (V) forms the first leg of a zigzag. The zigzag is extended further in the conformation shown (VI) for 3-ethyl-5-methylcyclohexanone, where both substituents are equatorial to the ring. The magnitude of the resulting rotatory strength is still large, even though the terminal methyl group is quite remote from the carbonyl. By contrast, conformation VII exhibits a very small, anti-octant value for R, in accord with the empirical behavior described by Coulombeau and Rassat.[19] It is seen from Figure 4 that the axial substituents on the 2-carbons give rise to strong two-center interactions, both with the 2-carbon and with the equatorial substituents and the carbonyl carbon. One notes that hydrogen atoms do indeed contribute strongly to the electric dipole transition moment, through C–H bonded or nonbonded, or H–H nonbonded terms. That hydrogen atoms have not been crucial to many applications of the octant rule can be ascribed to widespread cancelation of terms across local symmetry planes. However, they may play an important role in compounds where this is not the case, such as the twistanones.[44] Also significant is the moment induced in the C=O bond itself due to the overall dissymmetry of the wave function; the latter has the effect of mixing 2p$_x$ and 2p$_y$ orbitals into both n and π^* MO's. Strong two-center contributions also occur at the 3-equatorial positions, and in those other atoms and bonds that lie along Kirk and Klyne's "primary zigzag". Finally, one notes that direct interactions with the carbonyl oxygen are negligible in these compounds.

Figure 5 shows the same data, after account is taken of cancelation of terms across the X–Z plane, which is a symmetry plane in the parent, unsubstituted cyclohexanone. It now becomes apparent that the overall transition moment is heavily determined by the C=O bond moment, the terms connecting the carbonyl C with the 2- and 3-carbons, and the dissymmetry of the 3-carbon one-center terms. Additional effects come in strikingly in structures V, III, and VI, which extend the primary zigzag. By contrast, structure VII in particular shows an almost total lack of dissymmetry in the orbitals involved. The C=O bond moment in all these cases carries the same sign as the overall rotatory strength.

For purposes of comparison with the cyclohexanones, we have computed the rotatory strengths of Snatzke's two 3-methylated adamantanones (VIII and IX).[17] Table I shows the good agreement, both with the experimental $\Delta\epsilon$ values, and with the calculations on the corresponding methylcyclohexanones. The dimethyl- and trimethylcyclohexanones (X and XI) are also in good agreement with experiment. To the extent that additivity of contributions from perturbing groups is valid, the R value for 2,5-dimethylcyclohexanone (X) should be near 16.7 + 4.7 = 21.4. The calculated value of +18.6 is within acceptable limits. Similarly, one could obtain 16.7 + 4.7 + 10.2 = +31.6 for 2,2,5-trimethylcyclohexanone (XI), again acceptably close to the computed R = +25.8. One should note that the experimental values of $\Delta\epsilon$ are no more accurately additive (+2.0 vs. +0.9 for the summed terms).

We have computed rotatory strengths for all the *cis*- and *trans*-decalones and their monomethyl derivatives for which data are available.[22] The signs of R for the trans compounds agree with experiment except for *trans*-9-methyl-1-decalone (XIII). We predict that the addition of the methyl group to the parent decalone (XII) shifts the rotatory strength toward more positive values, in accord with one's expectation for a 2-axial methyl group, but our method evidently underestimates the shift. Comparing the calculated rotatory strengths for structures II and V, and the differences for (XI − X) and (XIII − XII), we see that there appears to be a systematic decrease in the magnitude of the contribution from a 2-axial methyl group, as the number of electrons in the molecule increases. If we had simply added the methyl group increment of II or V to the rotatory strength of XII, we would have obtained a value in agreement with experiment. Since we took over the Del Bene–Jaffé parameterization for this study without change, the effect of further variations in the semiempirical values ought to be, and remains to be, explored. In the 10-methyl derivative (XIV), the weak "anti-octant" effect of the 3-axial methyl group is computed correctly (cf. structures IV and IX). The latter effect is less sensitive to the size of the basis set, reflecting perhaps the much smaller n and π^* orbital electron densities at this position. Predictions for the corresponding *trans*-2-decalones are in line with experiment, except that we predict the 9-methyl derivative (XVI) to have a slightly smaller *R* value than the parent decalone (XV), contrary to the prediction of Kirk and Klyne[22] (no experimental data are available). In view of the "anti-octant" effect generally observed for a 3-axial methyl group, our results appears reasonable. The 10-methyl derivative (XVII) gives a rotatory strength nearly identical with that of its parent, as one expects due to the location of the methyl group astride one of the carbonyl symmetry planes. The factor of 2 variation in the experimental results for these two compounds is somewhat surprising when viewed in this light.

The *cis*-decalones are not conformationally rigid, having two distinct all-chair conformations accessible to them. Thus conformational equilibria may affect the observed CD. Our calculations for the conformers XVIII and XIX of *cis*-10-methyl-2-decalone agree well with the predictions of Kirk and Klyne, based on their empirical increments for different rings. NMR experiments[45] suggest a ratio of 70% XIX and 30% XVIII. If this ratio is applied to the calculated *R* values of −9.7 and −29.0, respectively, one obtains an "observed" *R* of −15.5, which correlates well with the observed $\Delta\epsilon \approx -0.3$. Moffitt et al.,[3] however, predict opposite signs for the two conformers, and are thus led to favor XVIII on the basis of the observed negative CD. It should be added that the *cis*-decalones have never fit well into the simple octant rule picture.[22] Kirk and Klyne assign positive $\Delta\epsilon$ values to both conformers of *cis*-10-methyl-1-decalone (XX and XXI), whereas we calculate a strongly negative *R* for XXI. Nearly the whole second ring is located in a front (−) octant if one assumes a surface like that of Coulombeau and Rassat.[19] One of the C_7 hydrogens in this conformation comes quite close to the position of a methyl hydrogen in Lightner and Chang's front octant compound,[1] which shows a large (−) CD. The observed $\Delta\epsilon$ of $\approx$0.3 would indicate that XX is strongly favored in our model, as opposed to the conclusion reached by Kirk and Klyne. The original prediction for this compound was that the XX conformer should be favored,[3] but these authors do not seem to have considered the possibility of front-octant effects for this compound. Our calculated values for 9-methyl-*cis*-1-decalone in the two forms XXII and XXIII agree with the predictions of Kirk and Klyne, except that our predicted *R* value for XXIII is somewhat smaller than their predicted $\Delta\epsilon$ value would indicate. In general, our estimates of front-octant effects are larger than theirs, but more in accord with the observations of ref 1. Note that, apart from the methyl group, structures XX and XXIII are enantiomeric, as are XXI and XXII.

Finally in this context, we quote rotatory strengths we have calculated for two compounds in which the dissymmetric methyl group is replaced by a fluorine atom. We have assumed a C–F bond length of 1.38 Å; all other structural and energetic parameters are the same. Fluoroacetone and 3(e)-fluorocyclohexanone were taken in conformations analogous to structures V and III, respectively. The calculated rotatory strengths were respectively −4.6 and −24.7, in accord with the observed "anti-octant" sign.[7] The sign reversal is traced, in our computations, to a change in the sign of mixing $2p_x$ and $2p_y$ AO's in the carbonyl group, and, for the cyclohexanone compound, an oppositely signed one-center term on the carbon bearing the fluorine atom. Other terms differ in magnitude from the corresponding ones in structures III and V, but not in sign.

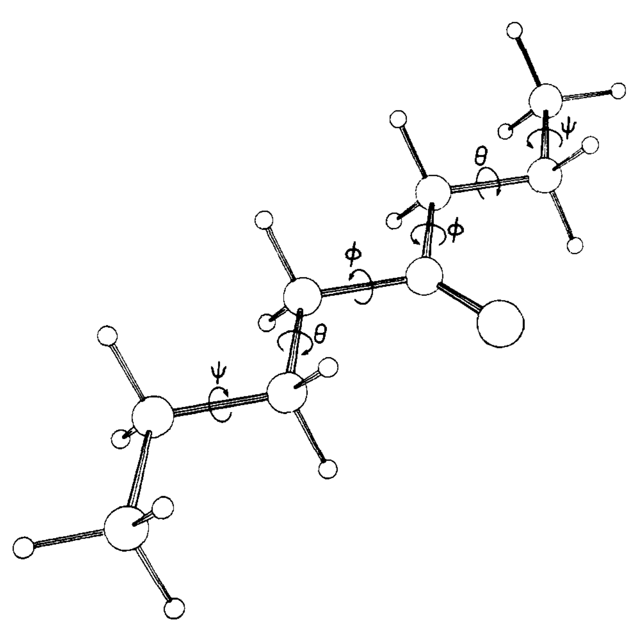

Figure 6. Torsional angles and sense of twist used for flexible model compounds. The *X*–*Z* plane of symmetry is maintained except for the dissymmetric methyl group and its antipodal hydrogen.

The Nature of the Third Nodal Surface. In order to explore the shape of the "third surface" of the octant rule, we chose several aliphatic ketones, each with one more carbon atom on one side of the carbonyl group than on the other. The molecule could be twisted in such a way that the only source of chirality would be the "extra" methyl group on the chain. Thus the rotatory strength could be calculated as a function of the position of this methyl group, and a surface constructed. By twisting both sides of the molecule in such a way as to maintain a plane of symmetry save for the terminal methyl group, the effect of the latter may be isolated insofar as possible. The molecules chosen were methyl ethyl ketone (MEK), ethyl propyl ketone (EPK), and propyl butyl ketone (PBK). In Figure 6 we show the conventions adopted for the torsional angles varied for the several compounds. All angles equalling zero means the fully extended, staggered conformation shown in the figure.

Rotatory strengths were calculated for all conformations of MEK and EPK at 30° increments of the torsional angles, such that the chiral methyl group remained in the upper left $(+X, +Y)$ quadrant. Selected conformations of PBK were also chosen, although a complete search of the torsional angle space was not feasible. The results are shown in Table II as a function of torsional angle; the Cartesian coordinates of the methyl carbon are also shown. The methyl group was found to lie within a range delimited by $X \leq 3.4$ Å, $Y \leq 5.0$ Å, and -3.6 Å $\leq Z \leq +1.8$ Å. We found the largest positive values of *R* along a band ±30° away from the primary zigzag conformations of Kirk and Klyne.[22]

Figure 7 represents an attempt at depiction of the regions of sign change. There are several important features to be seen. The first is that the primary sign-change region, the "third surface", is *convex* outward in the $+Z$ direction.[46] At first glance, this would appear to contradict the empirical results of Coulombeau and Rassat,[19] who based their concave surface on the "anti-octant" effects associated with the 3-axial position, as in structure IV, and the position of the dissymmetric methyl group in structure VII. Our surface, however, cuts just behind

Table II. Rotatory Strengths of Model Compounds as a Function of Torsional Angles and Cartesian Coordinates of Methyl Carbon

	Angles, deg				Coordinates, Å		
Compd	ϕ	θ	ψ	R	X	Y	Z
MEK	30			+17.1	0.73	2.40	−0.16
	60			+33.1	1.26	2.10	−0.59
	90			+35.5	1.45	1.68	−1.19
	120			+18.8	1.26	1.26	−1.78
EPK	0	30		+6.2	0.73	3.66	−0.73
	0	60		+9.6	1.26	3.35	−0.30
	0	90		+2.1	1.45	2.93	0.30
	0	120		−36.5	1.26	2.52	0.89
	0	150		−59.7[a,c]	0.73	2.21	1.32
	30	0		+8.3	0.73	3.66	−1.05
	30	30		+13.2	1.39	3.33	−1.19
	30	60		+13.3	1.94	2.86	−1.00
	30	90		+4.9	2.23	2.37	−0.51
	30	120		−8.9	2.18	1.98	0.14
	30	150		−87.2[a]	1.81	1.82	0.77
	30	180		−97.8[a,c]	1.21	1.91	1.22
	30	210		−89.0[a,c]	0.55	2.24	1.36
	30	240		+11.0[a]	0.0	2.71	1.16
	30	270		+6.2[d]	−0.29	3.20	0.68
	30	300		−1.5[d]	−0.24	3.59	0.03
	30	330		+1.9	0.13	3.75	−0.60
	60	0		+15.4	1.26	3.35	−1.48
	60	30		+17.2	1.68	2.86	−1.86
	60	60		+14.6	2.10	2.24	−1.88
	60	90		+5.6	2.40	1.65	−1.52
	60	120		−4.6	2.52	1.26	−0.89
	60	150		−10.4	2.40	1.17	−0.15
	60	180		−50.9	2.10	1.40	0.49
	60	210		−58.6	1.68	1.89	0.88
	60	240		−20.9	1.26	2.52	0.89
	60	270		+7.5	0.95	3.10	0.53
	60	300		+7.8	0.84	3.49	−0.10
	60	330		+10.9	0.95	3.59	−0.84
	90	0		+19.8[b]	1.45	2.93	−2.07
	90	30		+18.4[b]	1.52	2.37	−2.56
	90	60		+14.2	1.69	1.65	−2.71
	90	90		+5.4[b,c]	1.94	0.98	−2.47
	90	120		−3.0[b,c]	2.18	0.53	−1.92
	90	150		−8.4[b,c]	2.36	0.43	−1.19
	90	180		−2.2[b,c]	2.42	0.70	−0.49
	90	210		−4.2[b]	2.36	1.27	0.0
	90	240		−6.5[b]	2.18	1.98	0.14
	90	270		+6.8[b]	1.94	2.66	−0.10
	90	300		+13.6	1.69	3.10	−0.65
	90	330		+17.7	1.52	3.20	−1.38
3(e)-Methyl (III)	120	0		+16.7[e]	1.26	2.52	−2.67
3(a)-Methyl (IV)	120	240		−7.0[e]	2.52	1.26	−0.89
PBK	0	0	30	+0.5	0.73	4.92	−0.16
	0	0	45	+0.4	1.03	4.78	−0.35
	0	0	90	−1.7	1.45	4.19	−1.19
	0	0	120	−0.2	1.26	3.77	−1.78
	0	60	0	+4.0	1.26	4.61	0.59
	0	60	45	+4.8	1.89	3.81	1.03
	0	60	90	+3.3	2.40	2.91	0.63
	0	60	150	+3.2	2.40	2.42	−0.74
	0	90	0	+3.6	1.45	4.19	1.19
	0	90	30	+3.2	1.52	3.62	1.67
	0	90	60	+0.5	1.69	2.91	1.82
	0	90	90	−7.9	1.94	2.24	1.58
	0	90	120	−4.5	2.18	1.79	1.02
	0	90	150	−3.9	2.36	1.69	0.30
	0	90	180	+10.6	2.42	1.96	−0.40
	0	90	270	+0.3	1.94	3.91	−0.79
	0	120	0	−3.4	1.26	3.77	1.78
	30	30	120	−1.4	2.40	2.53	−2.03
	30	45	120	−1.8	2.72	2.09	−1.66
	60	45	90	+2.4	2.92	1.50	−2.39
	90	0	0	+13.6	2.90	3.35	−2.37

Table II (*Continued*)

Compd	Angles, deg			R	Coordinates, Å		
	ϕ	θ	ψ		X	Y	Z
	90	0	90	+7.8	1.45	2.52	−3.56
	90	0	300	+8.9	2.18	4.08	−1.34
	90	0	330	+11.8	2.71	3.77	−1.78
	90	270	0	+2.9	3.39	3.07	−0.40
	90	330	90	+7.9	1.30	3.55	−2.86
Structure VI	120	0	0	+12.5[e]	2.52	2.52	−3.56
Structure VII	120	0	240	−0.6[e]	1.26	3.77	−1.78

[a] O-H distance less than 2.0 Å. [b] H-H distance less than 1.8 Å. [c] Severely strained (O-H less than 1.75 Å; H-H less than 1.6 Å). [d] Methyl carbon in lower quadrant. [e] Cyclohexanone derivatives included for comparison.

Table III. Calculated Rotatory Strengths of 1-Aminopentan-3-one and Principal Contributions to $\langle n|\nabla_z|\pi^*\rangle$ Which Change Appreciably as the Torsional Angle of Nitrogen Lone Pair Is Varied

		Contributions to $\langle n|\nabla_z|\pi^*\rangle$, $\times 10^4$ au					
Angle τ, deg	$R_{n\to\pi^*}$	C*-O	C_α-C*	C_β-C*	N-C_β	C_β(1-ctr.)	N(1-ctr.)
0	+30.2	48	58	28	29	17	19
45	+25.2	36	46	23	18	23	25
90	+6.6	7	28	19	16	17	11
135	+0.9	1	29	20	25	8	8
180	+6.2	10	37	20	26	9	6
225	+2.1	2	27	19	21	11	2
270	+2.3	2	26	24	27	6	2
315	+18.7	31	48	30	35	7	3

the 3-axial position. The locations of the "anti-octant" axial methyl group of adamantanone IX[17] and the 2-*exo*-methyl group of bicyclo[2.2.1]heptan-7-one[18] coincide with this region. The second and more striking feature is the existence of a "pocket" of negative sign right at the location referred to for VII! Thus, the octant diagram shown in Figure 7 can serve to explain some observed "anti-octant" effects, and in fact will accommodate the data of Coulombeau and Rassat.[19] We also predict a second "pocket" above and in front of the 3-equatorial position. Since these areas can be reached through more than one set of torsional angles, it seems unlikely that they can be ascribed to angle effects alone. Indeed, the regularity of the spatial distribution of signs and magnitudes associated with the position of the methyl group, as well as the regularity seen as a function of angle alone, suggest that both spatial and angle effects play a part. By way of contrast, when the simple perturbation model[8,14] is applied to the determination of the third surface, only a slight, rearward curvature is observed, for X and $Y \leq 2.5$ Å.

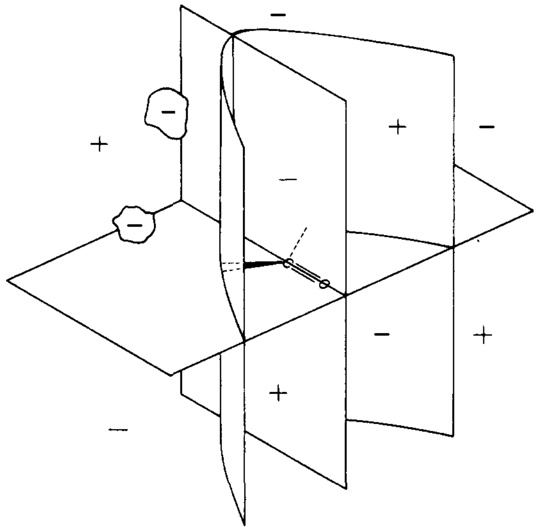

Figure 7. Schematic representation of the sign change regions computed for the carbonyl $n \to \pi^*$ rotatory strength. The nodal surface as we have computed it intersects the Y-Z plane approximately along the line $Y = Z + 2$. The two other regions of negative sign (weak CD) are centered about the points (1.3, 3.9, −1.4) and (2.5, 2.2, −1.8).

Nitrogen Lone Pair Orientation in Amino Ketones. As a final example of the dependence of rotatory strength on torsional angles, we consider the orientation of the nitrogen lone pair in amino ketones relative to the carbonyl group. These compounds were analyzed by Hudec,[23] and formed the basis for his original "zigzag" proposal. The orbital interactions in these molecules were thoroughly discussed by Levin et al.,[47] and the sensitivity of rotatory strength to lone pair orientation was mentioned in passing. To their analysis we can add our own calculations, which confirm this sensitivity and show as well the changes in the electric dipole transition moment as the torsional angle is changed.

In Figure 8 we show the basic conformation we have chosen of 1-aminopentan-3-one, with $\phi = 90°$, $\theta = 0°$, and τ to be varied. This conformation lies near the primary zigzag while keeping steric strain to a minimum. When $\tau = 0°$, the lone pair extends the zigzag, i.e., is trans to the C_α-C_β bond. Rotatory strengths were calculated at 45° increments of τ, and the results were analyzed into atomic contributions as before. Table III shows the calculated values of R and only those terms in $\langle n|\nabla_z|\pi^*\rangle$ that change as the angle τ is varied. It is seen that the ethyl side of the molecule remains virtually unchanged, while large changes are induced along the zigzag as the lone pair is rotated. The most dramatic changes occur in the carbonyl bond, reflecting the sensitivity of mixing of $2p_x$ and $2p_y$ orbitals to lone pair orientation. To compare the effect of methyl group rotation, we repeated the calculations for CH_3

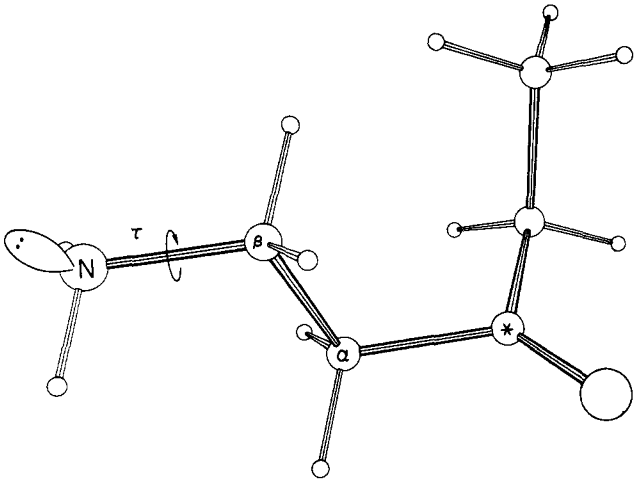

Figure 8. 1-Aminopentan-3-one, in the conformation chosen for the calculation with $\phi = 0°$, $\theta = 0°$, and (in this figure) $\tau = 0°$. Atoms are labeled to refer to Table III.

replacing NH_2. Rotatory strengths varied only between +19.8 and +20.6, which is negligible when compared with the variation in the amino ketone.

Summary and Conclusions

We have shown that the CNDO/S method is capable of yielding rotatory strengths for ketones that correlate well with experiment. We have also shed light on Kirk and Klyne's primary zigzag hypothesis, and on Hudec's analysis of the effects of orientation of the nitrogen "lone pair" in amino ketones. If cautiously applied, we believe the method can be of use in settling questions of absolute configuration, particularly if the parameters are further optimized for optical activity calculations.[48] The relative simplicity of the method has made possible an exploration of the third nodal surface. The results are surprising, in that the surface is convex when viewed from the carbonyl carbon toward the oxygen, and isolated, oppositely signed "pockets" also appear, yet the results agree with experiment where comparisons can be made. The forward curvature of the third surface is reminiscent of the surface derived by Höhn and Weigang[13] for an anisotropic perturbing group, but the more limited region of space we have explored inhibits a more detailed comparison. We are attempting to design optically active ketones with which to test the prediction of additional sign-change regions *behind* the third surface. We have also applied the method to a number of bridged-ring ketones, including methyl bicycloheptanones, bicyclooctanones, and twistanones; the experimental and theoretical results will be discussed in a subsequent paper.[49]

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(49) NOTE ADDED IN PROOF. Since this article was accepted, we have discovered an error in the magnitude (*but not the signs*) of the calculated rotatory strengths, which reduces the reported magnitudes by about 10–15%. The corrected value for IV, for example, is −6.1. The error occurs in the use of the overlap matrix from the CNDO/S program in computing the two-center magnetic moment integrals between heavy atoms. In the QCPE version, the local two-center $(2p\pi|2p\pi)$ overlaps incorporate the κ parameter ($\kappa = 0.585$), and are thus not the true overlap integrals. In our study, however, the magnetic moment of the $n \rightarrow \pi^*$ transition is dominated by the one-center terms on the carbonyl group, and the sign of the rotatory strength is determined by the electric moment; our conclusions are therefore unaffected.