In the broader view it must be recognized, however, that anything like exact correspondence between the extended Hückel and explicit electron repulsion methods such as the CNDO variations should not be expected. It is not reasonable to expect the equality expressed in eq 28 to generally hold, especially in the quest for determination of optimum structures where nearest neighbor bond lengths are continuously varied. In the event that the equality does not hold, the prescriptions adopted to date for charge redistribution in the EH methods, which are entirely dependent upon isolated atom properties, i.e., the valence-state ionization potentials and electron affinities, cannot satisfactorily reproduce the repulsion effects which are explicitly included in such as the CNDO methods. The scope of difficulty in defining meaningful separations of the total energy into orbital energy and repulsion contributions and construction of correlations between the orbital energies and Walsh's rules indicated here are further illustrated in several recent references.[17,21] Allen

and coworkers[5,17b] have, however, shown that clean cancellation of the extra-orbital effects are not necessary in order to extract information on equilibrium geometry.

Despite this, since just about the same amount of computational effort is required in application of any charge redistribution corrected EH method as for the CNDO methods, there seems to be little reason to prefer the former over the latter when structural information is sought. Distinction between the EH and KEH methods should be drawn on all previous accounts, however; useful and conceptually important separations of the kinetic and potential energy terms have been obtained in the KEH method. Development of techniques for the introduction of explicit repulsion and Coulomb integral effects[22] which are consistent with this separation and manage to avoid the dilemma implicit in eq 28, and its foundations would still appear to be a desirable goal both practically and for quantum chemical content.

(21) See also, G. Blyholder and C. A. Coulson, *Theor. Chim. Acta*, 10, 316 (1968); W. A. Bingle, "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 191; C. E. Wulfman, *J. Chem. Phys.*, 31, 381 (1959).

(22) S. Ehrenson, *Theor. Chim. Acta*, 10, 209 (1968).

The Anisotropy Factor of Optically Active Ketones

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Abstract: A simple theory for calculating the anisotropy factor $g = 4R_{0i}/D_{0i}$ of optically active ketones is developed. The theory is checked against a set of β-equatorial substituted adamantanones and methyl-substituted cyclohexanones. The dynamic coupling model parameter Θ_{0i}, the ketone transition electric quadrupole moment, is estimated to be 1.5×10^{-25} cgs from data obtained with correction for vibronic coupling. It is determined, independent of the model, that the β-equatorial substituted adamantanones have nonvibronically coupled transition electric dipole moments that have dominant Z polarization (i.e., $C{=}O$ axis polarization). The same conclusion obtains from the model calculations. The calculations on substituted cyclohexanones for the differential value of their Y-polarized moment relative to their Z moment compare well with experimental values. Consideration of anisotropy factors would seem a means of correcting the inherent bias in ketone rotatory strength calculation to only Z components of the transition electric dipoles.

E arly studies of optical activity defined and utilized the wavelength-dependent anisotropy factor $g(\lambda) = \Delta\epsilon(\lambda)/\epsilon(\lambda)$ as a useful comparison of electronic transition circular dichroism to ordinary absorption. Kuhn, Mathieu, and others[2-5] used g vs. λ plots to characterize various electronic transitions. The anisotropy factor was often found to be constant throughout a single transition. Its variation was taken to denote a change of transition in that interval.

Later theoretical work has largely abandoned the concept of an anisotropy factor as a detailed function of wavelength. Condon[6] first defined the factor as proportional to the ratio of integrated intensities.

(1) NASA Predoctoral Fellow.
(2) (a) W. Kuhn, *Trans. Faraday Soc.*, 26, 299 (1930); (b) *Z. Physik. Chem.*, B8, 286 (1930).
(3) W. Kuhn and H. L. Lehmann, *ibid.*, 18, 32 (1932).
(4) J. P. Mathieu, *Ann. Phys.*, 3, 371 (1935).
(5) T. M. Lowry, "Optical Rotatory Power," Dover Publications, New York, N. Y., 1935, p 393.
(6) E. U. Condon, *Rev. Mod. Phys.*, 9, 432 (1937).

$$g_{0i} = 4R_{0i}/D_{0i} \tag{1}$$

R_{0i} is the rotatory strength of the $i \leftarrow 0$ transition and is defined by

$$R_{0i} = \text{Im}\{\mathbf{\mu}_{0i} \cdot \mathbf{m}_{i0}\} = 0.24 \times 10^{-38} \int \frac{\Delta\epsilon(\lambda)}{\lambda} d\lambda \quad \text{(cgs)} \tag{2}$$

where $\mathbf{\mu}_{0i}$ and $\mathbf{m}_{i0}$ are the electric and magnetic dipole transition moments, respectively, λ is the wavelength, $\Delta\epsilon(\lambda) = \epsilon_l(\lambda) - \epsilon_r(\lambda)$, $\epsilon_l(\lambda)$ and $\epsilon_r(\lambda)$ are the decadic molecular extinction coefficients for the left and right circularly polarized light, and the universal constants have been evaluated to give cgs units. D_{0i}, the dipole strength of the transition, is defined by

$$D_{0i} = \mathbf{\mu}_{0i} \cdot \mathbf{\mu}_{i0} = 0.96 \times 10^{-38} \int \frac{\epsilon(\lambda)}{\lambda} d\lambda \quad \text{(cgs)} \tag{3}$$

where $\epsilon(\lambda) = [\epsilon_l(\lambda) + \epsilon_r(\lambda)]/2$.
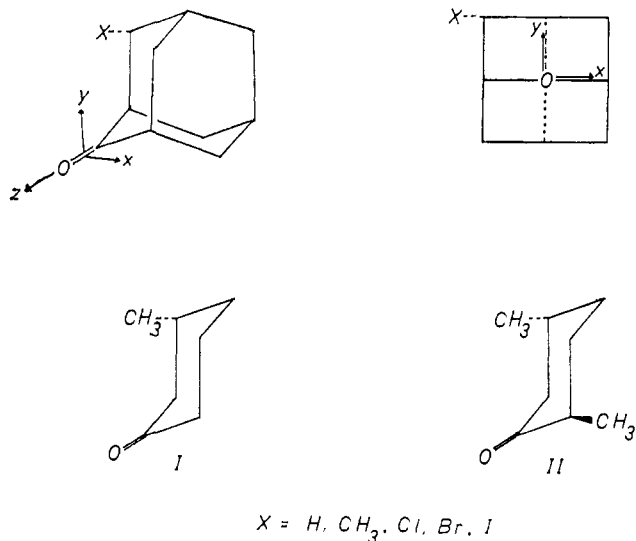
$X = H, CH_3, Cl, Br, I$

Figure 1. Structures of the compounds whose anisotropy factors are calculated along with the coordinate system chosen. β-Equatorial substituted adamantanone is shown in a projection diagram where the carbonyl lies on the Z axis. The upper portion corresponds to the substituted cyclohexanone structure.

Moffitt and Moscowitz more recently followed the integral definition, eq 1. For their case I,[7] they showed its equivalence to a constant $g(\lambda)$ within the span of a transition satisfying certain vibrational-electronic criteria. The work of Moscowitz and coworkers[8–10] on dimethyldibenzsuberone is a remarkable illustration of this case.

It has been suggested that the wavelength-dependent factor $g(\lambda)$ be developed more generally in theory for the information it contains.[11] But for case II or case III,[7,12] it is complex indeed and intimately related to the vibronic coupling in the absorption and in the circular dichroism. Instead, the work reported here utilizes the integral definition, eq 1. Furthermore, care is taken to account for any degree of vibronic coupling so that the left-hand sides of eq 2 and 3 may be referred to purely electronic descriptions of the molecules. Within such a scheme, a program for simple model calculations of molecular anisotropy factors can emerge.

A theory of dipole strength and hence of g factors for ketones is generally more complex in form than that for their rotatory strength.[9,13–16] The very recent synthesis of monosubstituted adamantanones[17] (Figure 1), however, provides data for molecules where a theory of dipole strength has minimal complexity. For such compounds a simple calculation of the "corrected" anisotropy factor is no more demanding than a corresponding simple calculation of the rotatory strength.[15] Indeed, an important check on the model parameters of

(7) W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).
(8) A. Moscowitz, K. Mislow, M. A. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).
(9) A. Moscowitz in *Advan. Chem. Phys.*, **4**, 67 (1962).
(10) A. Moscowitz in "Modern Quantum Chemistry," O. Sinanouglu, Ed., Academic Press, New York, N. Y., 1965, p 39.
(11) A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).
(12) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 3609 (1965).
(13) Y.-H. Pao and D. P. Santry, *J. Am. Chem. Soc.*, **88**, 4157 (1966).
(14) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 336 (1940).
(15) E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).
(16) G. Wagnière, *J. Am. Chem. Soc.*, **88**, 3937 (1966).
(17) G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968).

the latter calculation can obtain. In a few instances more complex systems can yield differential relationships between a given pair that are amenable to calculational check.

Theory

The 300-mμ transition of unconjugated ketones is electric dipole forbidden ($^1A_2 \leftarrow ^1A_1$; $n\pi^* \leftarrow 0$) in its local symmetry of C_{2v}. The entire molecular configuration and conformation can bring about a symmetry lowering that makes the transition electric dipole allowed. In perturbation terms one may say that an electric dipole has been "borrowed" by mixing states of the system components into the states of the ketone transition.

Such borrowing can be accomplished by the distortional conformation changes of molecular vibration. It can also obtain from the equilibrium position molecular symmetry. Varying fractions of the transition intensity in ketones is generated by each process.[12] A theoretical formulation of the electric dipole moment deriving alone from equilibrium position molecular symmetry lowering is the basis for most computations of ketone rotatory strength.

One may follow precisely the specific theory already developed for rotatory strength and develop the terms for dynamic coupling[15] between the system components. Neglecting terms which have to do with the anisotropy of the perturbers of the symmetric ketone system, there obtains a resultant expression for the dipole strength, eq 3, which is equivalent to each dipole moment $\mathbf{\mu}_{0i} = \mathbf{\mu}_{i0}$ being defined as

$$\mathbf{\mu}_{0i} = 3 \sum_{\sigma=1}^{N} R_\sigma^{-7} \bar{\alpha}_\sigma [(R_\sigma^2 Y_\sigma - 5X_\sigma^2 Y_\sigma)\mathbf{i} +$$

$$(R_\sigma^2 X_\sigma - 5X_\sigma Y_\sigma^2)\mathbf{j} + (5X_\sigma Y_\sigma Z_\sigma)\mathbf{k}]\Theta_{0i} \quad (4)$$

where $\bar{\alpha}_\sigma$ is the mean polarizability of the σ perturber, X_σ, Y_σ, and Z_σ are the coordinates of the σ perturber, $R_\sigma = (X_\sigma^2 + Y_\sigma^2 + Z_\sigma^2)^{1/2}$, Θ_{0i} is the XY component of the $n\pi^* \leftarrow 0$ transition quadrupole moment of the carbonyl chromophore,[18] and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are orthogonal unit vectors. Thus the electric dipole moment appears additive in the N substituent perturbers, like Platt's[19] spectroscopic moments for substituted benzenes, but the dipole strength equations in both instances have significant cross terms between the different isotropic substituents. Rotatory strength of ketones, on the other hand, is generally regarded as near additive in the substituents.

The net effect of cross terms produces an important result. It is that large collective components (*e.g.*, the ring of a cyclic ketone) can produce a vanishing dipole strength or one which appears to arise from a vector dipole moment with simple polarization. Thus the dipole strength from eq 3 and 4 will satisfy the relations that must derive from the total molecular symmetry.

Important to our considerations is that the perturbers that make up the cage structure of adamantanone collectively belong to the C_{2v} point group. As a result, their net contribution to the dipole strength vanishes, as well as that of their cross terms with any single additional perturber. In the case of chair-form cy-

(18) The parameters $\Theta_{0i} = \Theta_{0m}{}^{XY}(A)$, and $m_{i0} = -im_{m0}{}^Z(A)$ of ref 15.
(19) J. R. Platt, *J. Chem. Phys.*, **17**, 263 (1951).

clohexanone which belongs to the C_s point group, eq 4 gives an electric dipole moment with pure X polarization in our coordinate system (Figure 1, also that of ref 15). Indeed, by descent in symmetry from C_{2v} to C_s with $\sigma_v(YZ)$ retained as σ_h, the A_2 representation goes to A''. The coordinate which is the basis function for A'' then corresponds to the X axis of our Figure 1.

β-Equatorial Substituted Adamantanones

The β-equatorial haloadamantanones (Figure 1) display a relationship between ordinary absorption and circular dichroism intensities which can be interpreted without recourse to a specific theory. Figure 2 is a variation on a plot first obtained by Snatzke and Eckhardt.[17] It gives the rotatory strength vs. the square root of a corrected dipole strength of the 300-mμ transitions of the β-equatorial haloadamantanones, β-equatorial methyladamantanone, and unsubstituted adamantanone. The dipole strength of adamantanone must be regarded as purely vibronically coupled within the usual spectral assignment of $^1A_2 \leftarrow {}^1A_1$. Subject to later refinement, this vibronically coupled intensity is considered to be constant throughout this series of compounds. The corrected dipole strengths of Figure 2 were obtained by substracting the experimentally determined dipole strength of adamantanone[20] from the dipole strengths of the substituted adamantanones.

It follows then from eq 2 and 3 that the limiting slope (see Appendix) of the line in Figure 2 is related to purely electronic descriptions of the transition moment components according to

$$\frac{\Delta R_{0i}}{\Delta D_{0i}^{1/2}} = m_{i0}\left[1 + \left(\frac{\mu_{0i}^X}{\mu_{0i}^Z}\right)^2 + \left(\frac{\mu_{0i}^Y}{\mu_{0i}^Z}\right)^2\right]^{-1/2} = $$
$$0.69 \times 10^{-20} \quad \text{(cgs)} \quad (5)$$

Besides the special disposition of vibronically coupled intensity in the dipole strength, eq 5 makes the usual assumption that the ketone magnetic transition dipole moment m_{i0}[18] retains pure Z polarization.[21] It follows from the equation that a minimum value for the magnetic transition dipole moment is the slope value, 0.69×10^{-20} cgs units. Nonzero electric dipole components in the X and Y directions decrease the slope value resulting from a given constant m_{i0}.

A reconsideration of vibronic coupling leads to the following conclusions. Replacement of the constant vibronically coupled dipole strengths by a steady increase of vibronically coupled dipole strength, the variation expected with increasing substituent perturbation, would increase the slope shown in Figure 2 and more satisfactorily place its β-equatorial iodoadamantanone point. Only a suspiciously large degree of positive rotatory strength arising from vibronic coupling would alter the slope value from the conservative, minimum value for m_{i0} that it seems to represent.

Experimental values for the magnetic transition dipole moment m_{i0} of ketones have been determined in the work of Moscowitz and Mislow[8–10,22] on dimethyl-

(20) The dipole strength of adamantanone was measured to be 3.45×10^{-38} cgs which agrees with the extrapolated value of Snatzke and Eckhardt (see ref 17).

(21) The calculations of ref 13 especially examine this point.

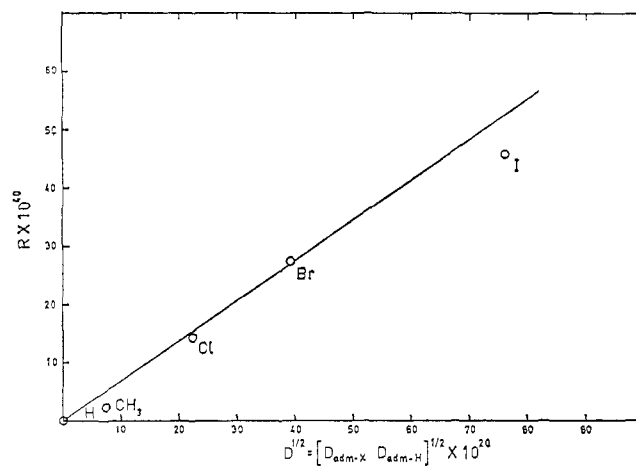(22) (a) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and

Figure 2. Experimental relationship[17] between the rotatory strength and the square root of the vibronically corrected dipole strength of various β-equatorial substituted adamantanones.

dibenzsuberone (DMDS) and of Mason[23] on cyclopentanone systems. The C_2 symmetry of the molecules assures that the nonvibronically coupled electric and magnetic transition dipoles are both purely Z polarized for the 300-mμ transition.

The most recent determination of the rotatory strength of DMDS[22] yields, on comparison with the dipole strength, a value of m_{i0} of 1.1×10^{-20} cgs units. The dipole strength D_{0i} of DMDS is about 90 times greater than that of β-equatorial chloroadamantanone, a scale on which vibronic coupling makes a negligible contribution. That this is the case is rather unambiguously supported by the case I correspondence of absorption and circular dichroism band shapes of DMDS, a relationship distinctly lacking in β-equatorial chloroadamantanone (λ^ϵ_{max} 295 mμ, $\lambda^{\Delta\epsilon}_{max}$ 306 mμ).[17] It seems nearly certain, however, that the very large perturbation-induced electric dipole moment of DMDS (0.5×10^{-18} cgs!) will be accompanied by significant modification of the zero-order value of m_{i0}.[24] The compounds of Mason's work[23] which are less highly perturbed give, on the other hand, a value of m_{i0} of 0.9×10^{-20} cgs units.

An experimental value of $m_{i0} < 1.0 \times 10^{-20}$ (cgs) compared to the slope value of eq 5 requires that more than 50% of the electric transition dipole strength induced by equilibrium position molecular symmetry lowering in the β-equatorial haloadamantanones is Z polarized. A value of $m_{i0} = 0.9 \times 10^{-20}$ (cgs) corresponds to 60% Z polarization. Considering the assumed constant vibronically coupled dipole strength, this percentage is likely underestimated. Such conclusions about the degree of Z polarization cannot be predicated on molecular symmetry as was the case for dimethyldibenzsuberone, but within the lowest C_1 symmetry of the substituted adamantanones must obtain accidentally; alternatively, within a perturbation

G. C. Hanson, J. Am. Chem. Soc., **90**, 4877 (1968); (b) K. Mislow, private communication.

(23) S. F. Mason, Mol. Phys., **5**, 343 (1962); Quart. Rev. (London), **17**, 20 (1963).

(24) In an attempt to determine whether this value of m_{i0} results from the choice of isooctane as a solvent, the absorption spectrum and circular dichroism were measured in dioxane. The ordinary absorption background correction[9] becomes so large in dioxane that sufficiently accurate dipole strength cannot be determined. On the other hand, the rotatory strength decreases by 5%.

Table I. The Calculated Anisotropy Factors of Various Ketones Compared to Their Experimental Quantities

	Methyl-	Chloro-	Bromo-	Iodo-
		—————Adamantanone—————		
D(exptl)[a]	4.04×10^{-38}	8.41×10^{-38}	18.93×10^{-38}	61.4×10^{-38}
R(exptl)[a]	2.41×10^{-40}	14.44×10^{-40}	27.6×10^{-40}	46.0×10^{-40}
g(exptl)[b]	0.164	0.116	0.072	0.032
D(theor)$/\Theta_{0i}^2$	2.49×10^{12}	4.64×10^{12}	7.57×10^{12}	17.70×10^{12}
$\%\ X$ (pol)	35.9	4.9	5.9	6.1
$\%\ Y$ (pol)	1.3	11.3	2.3	5.9
$\%\ Z$ (pol)	62.8	83.9	91.8	88.0
R(theor)$/m_{i0}\Theta_{0i}$	1.47×10^6	1.97×10^6	2.64×10^6	3.95×10^6
g(theor)Θ_{0i}/m_{i0}	17.08×10^{-7}	17.01×10^{-7}	13.91×10^{-7}	8.93×10^{-7}
Θ_{0i}(calcd)[c]	4.14×10^{-26}	10.4×10^{-26}	14.3×10^{-26}	16.1×10^{-26} [d]
m_{i0} (calcd)[e]	0.396×10^{-20}	0.706×10^{-20}	0.735×10^{-20}	0.728×10^{-20} [d]

[a] See ref 17. For the dipole strength, the Moffitt and Moscowitz definition was used rather than the Mulliken definition used in this reference. [b] Equation 1. The dipole strength of adamantanone ($D = 3.45 \times 10^{-38}$ cgs) was subtracted from the dipole strength of the substituted adamantanones. [c] Θ_{0i}(calcd) is given by $[R(\text{theor})g(\text{exptl})/R(\text{exptl})g(\text{theor})]^{1/2}$. [d] An extrapolated dipole strength ($D = 44.4 \times 10^{-38}$ cgs) was used from β-equatorial iodoadamantanone. The experimental dipole strength value gives $\Theta_{0i} = 18.1 \times 10^{-26}$ cgs, and $m_{i0} = 0.69 \times 10^{-20}$ cgs. [e] m_{i0}(calcd) is given by $[R(\text{theor})g(\text{theor})/R(\text{exptl})g(\text{exptl})]^{1/2}$.

description, one may suggest it obtains from the symmetry restrictions imposed on a particular electronic coupling mechanism between the symmetrical adamantanone and the added substituent.

Calculational Models

The detailed model implied by eq 4 can be examined for the symmetry-restricted characteristics it imposes on the moments borrowed by dynamic coupling. One may notice that the nodal surfaces for the terms coefficent to the unit vectors **i**, **j**, **k** are respectively the "X-anisotropy cone," the "Y-anisotropy cone," and the "octant planes" important in a theory of the optical activity of ketones.[15]
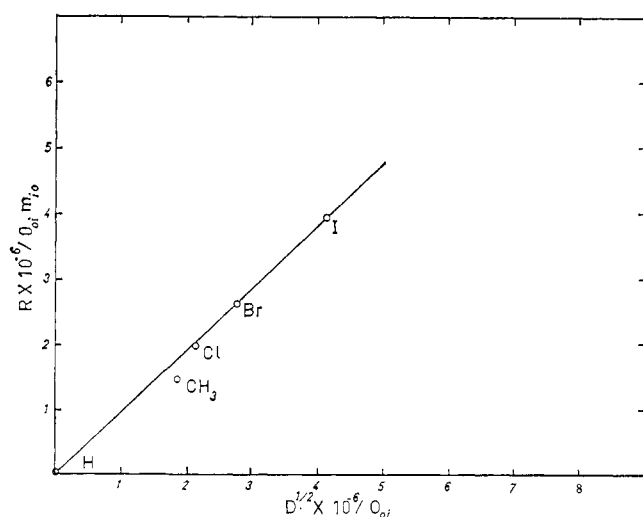

Figure 3. Calculated relationship between the rotatory strength and the square root of the dipole strength of various β-equatorial substituted adamantanones.

Table I gives the relative value of the calculated dipole strengths arising from these separate moments for β-equatorial methyl-, chloro-, bromo-, and iodoadamantanones. Idealized adamantane geometry was used with all angles tetrahedral and the following bond lengths (Å) were used: C–C, 1.54; C–H, 1.09; C–Cl, 1.78; C–Br, 1.92; C–I, 2.10. The origin of the coordinate system was taken to be at the midpoint of the

carbonyl bond, or 0.60 Å from the carbonyl carbon atom.

The results shown in Table I accord with the conclusions of the previous section. The calculations indicate that 84–92% of the dipole strength is Z-axis polarized. The calculations reflect the fact that the substituents lie quite near both the X- and Y-cone nodal surfaces.

The calculated rotatory strengths in Table I were obtained from eq 13 of ref 15. Figure 3 is the calculated theoretical plot equivalent to Figure 2. It is perhaps significant that β-equatorial methyladamantanone shows the same deviation in Figure 3 as in Figure 2. In Figure 3 it is clearly attributable to a very much smaller fraction of Z-polarized dipole strength.

Table I also shows calculations for pure electronic anisotropy factors of these compounds according to the equation

$$g = \frac{5}{3} \times$$
$$\frac{XYZR^7}{(R^2Y - 5X^2Y)^2 + (R^2X - 5XY^2)^2 + (5XYZ)^2}\frac{m_{i0}}{\alpha\Theta_{0i}}$$

(6)

The experimental anisotropy factors to which the calculated values are compared have been corrected for the constant vibronically coupled dipole strength used in Figure 2. Comparison of calculated and experimental values as conservatively corrected give the table values for m_{i0} and Θ_{0i}.

The slopes of Figures 2 and 3 give an average value of $m_{i0} = 0.725 \times 10^{-20}$ cgs for the haloadamantanones. The low value of m_{i0} of course represents a lower limit within the model's assignment of 84–92% of dipole strength to Z polarization rather than the 60% which would give 0.9×10^{-20} cgs unit. From similar considerations, it would appear that the degree of Z polarization for β-equatorial methyladamantanone is also overestimated by the model. There remain, however, the uncertainties of vibronically coupled dipole strengths.

It is apparent that derived values for m_{i0} depend only on experimental ratios. Furthermore, in a model for solvent effects where only the transition electric dipole is considered solvent sensitive, the slope of Figure 2 can be expected to be largely independent of such effects.

A value of Θ_{0i}, on the other hand, theoretically locates the position of the molecular points on the given slope of Figure 3. Evaluation of Θ_{0i} by comparison with Figure 2 may thus be highly solvent sensitive for some compounds.

Viewing the solvent effect as due to the polarizable medium competing with the polarizability of the admantanone substituent, the discrepancy between the value of Θ_{0i} for β-equatorial methyladamantanone and the β-equatorial haloadamantanone is quite understandable. The ratio of polarizability to volume of displaced solvent will stand somewhat as $\sim 1.1 \times 10^{-2}$ for the methyl substituent as compared to 1.7–1.9×10^{-2} for the halogen substituents.[25] The larger value for halogen substituents will represent a limit in which the polarizability of the displaced solvent is more negligible, the Θ_{0i} thereby representing more nearly solvent-independent values.

It is noteworthy that derived values give an $m_{i0}\Theta_{0i}$ for β-equatorial methyladamantanone that is in excellent agreement with that obtained from earlier work on alkyl-substituted ketones.[15] Thus a value of $\sim 2 \times 10^{-46}$ cgs seems a suitable adjusted rotatory strength parameter that will take account of measurement performed in solvents of ordinary refractive index.

One can also compare the results of calculated and experimental differential anisotropy factors. The dipole strengths of 3-methylcyclohexanone and 3,6-dimethylcyclohexanone would be indeed complex to calculate individually. On the other hand, the difference of dipole strengths of those two compounds does not contain many terms. This is so since the X components of dipole strength, due only to the 3-position substituent and the collective ring constituents, and the Z components of dipole strength, due only to the 3-substituent, will cancel precisely in the difference. The calculated differential dipole strength thus represents Y-component contributions arising from the 3- and 6-substituents, including their cross terms. The corresponding experimental differential dipole strength would have subtracted out a vibronically coupled strength common to the two compounds.

The rotatory strength is the same for both compounds, deriving from only the Z component of transition dipole moment. To take advantage of the simple difference of dipole strength expression, it is most convenient to compare calculated differences of the *reciprocal* anisotropy factors to experiment. The expression becomes

$$g_{\mathrm{I}}^{-1} - g_{\mathrm{II}}^{-1} = (D_{0,i}{}^{\mathrm{I}} - D_{0,i}{}^{\mathrm{II}})/4R_{0,i} \qquad (7)$$

where each of the ratios in eq 7 is an inverse of the form of eq 6. The ratio of m_{i0} and Θ_{0i} was taken from the table values for β-equatorial methyladamantanone.

$g_{\mathrm{I}}^{-1} - g_{\mathrm{II}}^{-1}$ (exptl)[26]	$g_{\mathrm{I}}^{-1} - g_{\mathrm{II}}^{-1}$ (theor)[27]
-8.6	-12

(25) Polarizabilities and Leonard–Jones radii for gaseous viscosity were taken from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p 950, 1110 ff. The effective substituent radii in solution can be expected to be much smaller but paralleling the gaseous values.

(26) Experimental differences of the reciprocal anisotropy factors of compounds I and II: N. L. Allinger, J. Allinger, L. E. Geller, and C. Djerassi, *J. Org. Chem.*, **25**, 6 (1960); W. P. Hayes and J. Timmons, *Spectrochim. Acta*, **21**, 529 (1965).

Other Coupling Mechanisms

Equation 4 and the calculations that have been carried out with it assume that dynamic coupling, as opposed to static coupling or charge transfer, is the dominant mechanism of perturbation of the zero-order independent systems. These latter models should be examined for a property of predicting dominant Z-polarized electric dipole strength in the β-equatorial haloadamantanones.

Electric transition dipoles accompanying charge-transfer electronic excitations arise principally from the change in static dipole moment accompanying the electron transfer from donor to acceptor.[16,28] To a first order of approximation, the coordinate positions of a perturber (e.g., $X = -2.04$ Å, $Y = 1.26$ Å, $Z = -2.93$ Å for Br) stand in ratios equal to the ratios of these dipole moments. The prediction of degree of Z polarization would not be unsatisfactory. The discussion of the appropriateness of this mechanism has been discussed at length elsewhere.[16,29]

For static coupling the equations analogous to eq 4 have, as the first nonvanishing terms

$$\mathbf{\mu}_{0i} = \sum_{\gamma} \sum_{\sigma=1}^{N} \frac{X_{\sigma} Y_{\sigma} \epsilon_{\sigma}(B) \Theta_{\gamma i}{}^{XY}(A) \mu_{\gamma 0}{}^{Z}(A) \mathbf{k}}{R_{\sigma}{}^{5}(E_i - E_{\gamma})} \qquad (8)$$

$(\gamma, A_1 \text{ state symmetry})$

$$\mathbf{\mu}_{0i} = \sum_{\gamma} \sum_{\sigma=1}^{N} \frac{X_{\sigma} Y_{\sigma} \epsilon(B) \Theta_{\gamma 0}{}^{XY}(A) \mu^{Z}{}_{\gamma i}(A) \mathbf{k}}{R_{\sigma}{}^{5}(E_0 - E_{\gamma})} \qquad (9)$$

$(\gamma, A_2 \text{ state symmetry})$

$$\mathbf{\mu}_{0i} =$$
$$\sum_{\gamma} \sum_{\sigma=1}^{N} \frac{\epsilon_{\sigma}(B) \mu_{\gamma 0}{}^{X}(A) \mu_{\gamma i}{}^{Y}(A)}{R_{\sigma}{}^{3}} \left[\frac{X_{\sigma}}{E_{\gamma} - E_0}\mathbf{i} + \frac{Y_{\sigma}}{E_i - E_{\gamma}}\mathbf{j} \right] \qquad (10)$$

$(\gamma, B_1 \text{ state symmetry})$

$$\mathbf{\mu}_{0i} =$$
$$\sum_{\gamma} \sum_{\sigma=1}^{N} \frac{\epsilon_{\sigma}(B) \mu_{\gamma 0}{}^{Y}(A) \mu_{\gamma i}{}^{X}(A)}{R_{\sigma}{}^{3}} \left[\frac{X_{\sigma}}{E_i - E_{\gamma}}\mathbf{i} + \frac{Y_{\sigma}}{E_{\gamma} - E_0}\mathbf{j} \right] \qquad (11)$$

$(\gamma, B_2 \text{ state symmetry})$

where $\epsilon_{\sigma}(B)$'s are the static charges of the σ perturber. The other extensions of notation are somewhat obvious and are fully defined in ref 15.

Recently Bouman and Moscowitz[30] have shown that the parameter $\Theta_{\gamma i}{}^{XY}$ (A) of eq 8 is sufficiently small for all suitable states such that the higher order octupole terms of the expansion dominate in eq 8. While this gives the empirically favored octant rule behavior for ketones, it only increases the disparity between levels of multipole expansion which induces Z polarization as opposed to X and Y polarization. Of course, whether or not the charge-dipole induced X- and Y-directed components may cancel and have resultants comparable and even smaller than charge-octupole-induced Z-directed components depends upon details about many higher states that are difficult to meaningfully define at this stage.

(27) Theoretical differences of the reciprocal anisotropy factors of compounds I and II.

(28) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

(29) A. Moscowitz, *Proc. Roy. Soc.*, **A297**, 40 (1967).

(30) T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, **48**, 3115 (1968).

Conclusions

It appears that a systematic study of anisotropy factors, but with careful attention to vibronic coupling effects, can yield important information. Any theory of optical activity should, in its broadest aspects, agree with the general characteristics and behavior of the anisotropy factors. In this way, a possibly prejudicial preoccupation with the Z component of the electric dipole moment of ketone $n\pi^* \leftarrow 0$ transitions is to be avoided. It seems that characteristics in this regard of even the simplest theories ought to be determined before more detailed theory is attempted.

There is also an important specific conclusion for the β-equatorial adamantanones. Insofar as the electric transition dipole moment is strongly Z polarized, these compounds (but less so for β-equatorial methyl-adamantanone) become an important "standard" set where vibronic coupling in the rotatory strength is minimal. The manner in which they have been treated in our work corresponds precisely to the case II limit of Moffitt and Moscowitz.[7,12] In compounds where decidedly less nonvibronically coupled moment lies parallel to the magnetic transition dipole, "allowed" character will compete less effectively with "forbidden" character, even to the extent of the latter becoming dominant.[12] Increasing attention to anisotropy factors in the future may help to delineate this condition.

Appendix

It may appear that the derived form of eq 5 is not unique. Further discussion may clarify this.

The problem may be considered one of five variables $(R, D^{1/2}, \mu_{0i}{}^X, \mu_{0i}{}^Y,$ and $\mu_{0i}{}^Z)$ and two implicit functional relationships connecting them. Taking R and $\mu_{0i}{}^Z$ to be dependent variables, one may write the total dif-

ferential of rotatory strength

$$dR = m_{i0}\left\{\left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{1/2}dD^{1/2} - \frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}d\mu_{0i}{}^X - \frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}d\mu_{0i}{}^Y\right\}$$

Alternatively, and to some advantage, a choice of variables $R, \mu_{0i}{}^Z, D^{1/2}, \mu_{0i}{}^X/\mu_{0i}{}^Z,$ and $\mu_{0i}{}^Y/\mu_{0i}{}^Z$ gives a total differential of rotatory strength, that is

$$dR = m_{i0}\left\{\left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{-1/2}dD^{1/2} - \left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{-1/2}\mu_{0i}{}^X d\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right) - \left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{-1/2}\mu_{0i}{}^Y d\left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)\right\}$$

For $\mu_{0i}{}^X/\mu_{0i}{}^Z = \mu_{0i}{}^Y/\mu_{0i}{}^Z = 0$ the two expressions are identical. In the case that $\mu_{0i}{}^X/\mu_{0i}{}^Z$ and $\mu_{0i}{}^Y/\mu_{0i}{}^Z$ approach some limiting finite value as $\mu_{0i}{}^Z$ goes to zero (as $\mu_{0i}{}^Z$ must for optically inactive unsubstituted adamantanone), then clearly the first representation of dR generally has three nonvanishing terms. On the other hand, the second representation for dR has only one nonvanishing term. Thus a plot of R vs. $D^{1/2}$ may be interpreted as having a limiting slope of

$$m_{i0}\left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{-1/2} = \left(\frac{\partial R}{\partial D^{1/2}}\right)_{\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z},\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}}$$

even with small changes in $\mu_{0i}{}^X/\mu_{0i}{}^Z$ and $\mu_{0i}{}^Y/\mu_{0i}{}^Z$.

For the second representation to continue to give a simple slope interpretation away from the "inactivity" limit, $\mu_{0i}{}^X/\mu_{0i}{}^Z$ and $\mu_{0i}{}^Y/\mu_{0i}{}^Z$ must be constants. More precisely it is only necessary that

$$\left[\left(\frac{\mu_{0i}{}^X}{\mu_{0i}{}^Z}\right)^2 + \left(\frac{\mu_{0i}{}^Y}{\mu_{0i}{}^Z}\right)^2 + 1\right]^{-1/2}$$

the square root of the fraction of Z-polarized dipole strength, be constant. This condition corresponds to a constant direction cosine between $\mathbf{\mu}_{0i}$ and $\mathbf{m}_{i0}$. That the experimental points extrapolate to the origin like the points of the calculated model where this condition is so gives support that this condition obtains sufficiently in this experimental case.