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An Expiscation of Structural–Vibrational Effects in Magnetic Circular Dichroism Spectra of Saturated Ketones[2]

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Abstract: It is now known (preceding paper in this issue) that totally symmetric static structural perturbations can alter the MCD intensity borrowed by nontotally symmetric vibrations in a forbidden transition. The effect is examined numerically with the aid of molecular orbital theory. A simple semiempirical stereochemical model is developed that handles the vibrational–structural interaction associated with substituent atoms at the α carbons in saturated ketones. The model is tested against the experimental MCD data (B values) for a wide variety of alkyl substituted saturated ketones (*trans*-2-decalones, cyclobutanones, acyclic ketones, cyclopentanones, bicyclo[2.2.2]octan-2-ones, cyclohexanones, and certain bridged ketones) and is found to work satisfactorily. The model also provides a useful extension of our earlier analysis of MCD-structural relationships. The revised protocol, within stated limitations, accounts reasonably well for the variation in MCD intensity with variation in structure.

While the keto group is one of the most widely studied chromophores, the diversity of structures to which it may be attached and the effects of substituents on its electronic structure continue to challenge chemists and spectroscopists. Since the near ultraviolet electronic transition, $n \rightarrow \pi^*$, is locally electric dipole forbidden but magnetic dipole allowed, chiroptical methods have been extensively used to gain structural information about both ground and excited states.[3-6] More recently, magnetic circular dichroism (MCD) spectra have been shown to be sensitive to the stereochemistry of ketones,[7] and certain aspects of the mechanisms involved have been investigated.[8-12] Here, and in the preceding paper,[2a] we recognize the importance of and investigate a previously neglected effect: the effect that totally symmetric structural perturbations have on the MCD intensity generated by nontotally symmetric vibrational perturbations. In the preceding paper we examined the general theory; here we continue with specific applications to the $n \rightarrow \pi^*$ ($^1A_1 \rightarrow {}^1A_2$) excitation in saturated ketones.

Theory

(A) Background. We rely heavily in this work on three earlier studies, two of which[9,12] concern the group theoretical interpretation of the MCD spectra of saturated ketones; the other[10] is an investigation of the vibronic coupling mechanism in formaldehyde.

Since the $n \rightarrow \pi^*$ excitation in ketones is locally symmetry forbidden, the intensity of the MCD spectrum associated with the transition is of second or higher order in perturbations that are nontotally symmetric in C_{2v}. Furthermore, the partial B values which result from perturbations belonging to different irreducible representations of C_{2v} are additive through second order.[12] In ref 9, we classified such perturbations as either structural (static) or vibrational. Physical arguments were presented which related the signs of the partial B values associated with the static and vibrational perturbations, and the signs of the vibrational contributions were determined from the MCD spectra of C_{2v} molecules such as formaldehyde and cyclobutanone. It was also shown that the then available data were in the large consistent with these arguments and inferences, provided that due consideration be given to possible changes in the vibrational contributions upon substitution.

Generally, we wished to focus attention on the static (structural) perturbations and we tended to make our detailed comparisons only on compounds which could reasonably be expected to have a constant vibrational contribution. Subsequently,[10] we presented the geometric perturbation (GP) method for the calculation of vibrational contributions to the B values of formaldehyde. With this tool, we have now reexamined some of our previous assumptions and find that revisions are needed. This reexamination was made necessary by the generation of new experimental data[13,14] that indicate that our previous analyses[9] failed to recognize the importance of a contribution associated with *totally symmetric* static perturbations.

The rationale for the subordination of totally symmetric structural perturbations in ketones (except for conformational stabilization effects) lay in the fact that nontotally symmetric perturbations are required for the generation of MCD intensity in a forbidden transition. However, as shown in the accompanying paper,[2a] if there is a nontotally symmetric vibrational perturbation operative, the totally symmetric static (structural) perturbations can exert a synergistic (or antienergistic) effect on the vibrational perturbations as regards the generation of MCD intensity. This effect appears in eq 22 of ref 2a as the B_r^{VS} terms.

It will be useful to have a single word for the concerted vibrational–structural perturbation that gives rise to the (B^V + B^{VS}) terms of eq 22, ref 2a. We suggest the word "vibruction", on the grounds that its functionality outweighs its cacophony.

As we shall see, the syn–anti energistic effect of the totally symmetric structural perturbations arises from an alteration of the efficacy of the vibronic coupling mechanism by which MCD intensity is borrowed in a forbidden transition. In molecular orbital terms, the alteration takes its origin in the delocalization of chromophoric MO's onto atomic centers other than those of the carbonyl group itself. It turns out that the effect is strongly dependent on the relative stereochemistry of the carbonyl group vis-à-vis nearby atomic centers and also upon the C_α–C–$C_{\alpha'}$ bond angle. This is in accord with previous observations made for MCD data on ketones.[8,11] It is also consonant with MO calculations, such as those given most recently by Bouman and Lightner,[15] in connection with natural optical activity, that suggest a multicenter origin for the transition moments in ketones.

(B) **Molecular Orbital Considerations.** Equation 22 of the preceding paper[2a] manifests the effect of totally symmetric static perturbations on vibrational contributions. However, that equation is numerically intractable as it stands, since its application requires detailed knowledge of the vibrational modes and of the manifold of excited electronic states. In seeking a numerically tractable model we need to review some previous results.[10]

The GP expression for the B value of a molecule with C_{2v} symmetry[10] is

$$B(\mathrm{A} \rightarrow \mathrm{J}) = \sum_r \left[B_r{}^0 + \sum_{\mathrm{K} \neq \mathrm{A,J}} B_r{}^1 \right] \tag{1}$$

where

$$\begin{aligned} B_r{}^0 &= \mathrm{Im}\{E_{\mathrm{JA}}{}^{-1} \langle \mathrm{J}|\boldsymbol{\mu}|\mathrm{A}\rangle_r \cdot [\langle \mathrm{A}|\mathbf{m}|\mathrm{J}\rangle_r \\ &\qquad \times (\langle \mathrm{J}|\mathbf{m}|\mathrm{J}\rangle_r - \langle \mathrm{A}|\mathbf{m}|\mathrm{A}\rangle_r)]\} \\ B_r{}^1 &= \mathrm{Im}\{E_{\mathrm{KJ}}{}^{-1} \langle \mathrm{J}|\boldsymbol{\mu}|\mathrm{K}\rangle_r \cdot [\langle \mathrm{A}|\mathbf{m}|\mathrm{J}\rangle_r \times \langle \mathrm{K}|\mathbf{m}|\mathrm{A}\rangle_r] \\ &\quad + E_{\mathrm{KA}}{}^{-1} \langle \mathrm{K}|\boldsymbol{\mu}|\mathrm{A}\rangle_r \cdot [\langle \mathrm{A}|\mathbf{m}|\mathrm{J}\rangle_r \times \langle \mathrm{J}|\mathbf{m}|\mathrm{K}\rangle_r]\} \end{aligned} \tag{1a}$$

and, for example,

$$\langle \mathrm{J}|\boldsymbol{\mu}|\mathrm{K}\rangle_r = \langle \mathrm{J}|\boldsymbol{\mu}|\mathrm{K}\rangle_0 + \left[\frac{\partial \langle \mathrm{J}|\boldsymbol{\mu}|\mathrm{K}\rangle}{\partial Q_r} \right]_0 \langle Q_r{}^2\rangle^{1/2} + \ldots \tag{2}$$

where

$$\langle Q_r{}^2\rangle = \hbar/4\pi\nu_r{}^0 \tag{2a}$$

and where Q_r and $\nu_r{}^0$ are the normal coordinate and frequency of the rth normal mode. Here a zero subscript indicates a quantity evaluated at the equilibrium geometry. For formaldehyde[10] $B_r{}^0$ was shown to be the largest term in eq 1, as it is for the case of the other ketone calculations which appear below. Furthermore, since the major contribution to $B_r{}^0$ arises from terms involving $\langle \mathrm{J}|\mu_z|\mathrm{A}\rangle_0$[10] ($|\mathrm{J}\rangle = |\mathrm{n}\pi^*\rangle$), we expand $B_r{}^0$ and keep only the leading term[16] involving $\langle \mathrm{J}|\mu_z|\mathrm{A}\rangle_0$.

$$\begin{aligned} B_r{}^0 \cong \mathrm{Im}\{E_{\mathrm{J,A}}{}^{-1} \langle \mathrm{J}|\mu_z|\mathrm{A}\rangle_0\, \hat{\mathbf{k}} \cdot [\langle \mathrm{A}|\mathbf{m}|\mathrm{J}\rangle_r \\ \times (\langle \mathrm{J}|\mathbf{m}|\mathrm{J}\rangle_r - \langle \mathrm{A}|\mathbf{m}|\mathrm{A}\rangle_r)]\} \end{aligned} \tag{3}$$

The GP wave functions[10] appropriate to the distorted molecular geometry are the electronic eigenstates evaluated at $Q_r = \langle Q_r{}^2\rangle^{1/2}$. If we use first order perturbation theory to express them in terms of the equilibrium states $|\mathrm{K}^0\rangle$ of ref 2a and ignore ground state mixing we obtain

$$|\mathrm{A}\rangle_r = |\mathrm{A}^0\rangle$$

$$|\mathrm{J}\rangle_r = |\mathrm{J}^0\rangle + \sum_{\mathrm{K}^0 \neq \mathrm{J}^0} \lambda_{\mathrm{KJ}}{}^r |\mathrm{K}^0\rangle \langle Q_r{}^2\rangle^{1/2} \tag{4}$$

where

$$\lambda_{\mathrm{KJ}}{}^r = \langle \mathrm{K}^0|H_r{}^{(1)}|\mathrm{J}^0\rangle / E_{\mathrm{JK}} \tag{4a}$$

and where

$$H_r{}^{(1)} = [\partial H_{\mathrm{e}}/\partial Q_r]_0 \tag{4b}$$

Insertion of eq 4 into eq 3 then gives

$$\begin{aligned} B_r{}^0 \simeq 2\,\mathrm{Im}\Big\{ & E_{\mathrm{JA}}{}^{-1} \langle \mathrm{J}^0|\mu_z|\mathrm{A}^0\rangle \hat{\mathbf{k}} \\ & \sum_{\mathrm{K}^0 \neq \mathrm{J}^0} \sum_{\mathrm{L}^0 \neq \mathrm{J}^0} \lambda_{\mathrm{KJ}}{}^r \lambda_{\mathrm{LJ}}{}^r \langle \mathrm{A}^0|\mathbf{m}|\mathrm{K}^0\rangle \\ & \times \langle \mathrm{J}^0|\mathbf{m}|\mathrm{L}^0\rangle \Big\} \langle Q_r{}^2\rangle \end{aligned} \tag{5}$$

In some instances it will facilitate the interpretive analysis to look at $B_r{}^0$ within the single configuration approximation and to concern ourselves with only the lowest lying nπ^*, nσ^*, and $\sigma\pi^*$ states. In such instances, eq 5 specializes to

$$\begin{aligned} B_r{}^0 \cong -4\,\mathrm{Im}\Big\{ & E_{\mathrm{n}\pi^*,\mathrm{A}}{}^{-1} \langle \mathrm{n}|\mu_z|\pi^*\rangle_0 \\ & \times \frac{\langle \sigma^*|H_r{}^{(1)}(\mathrm{b}_1)|\pi^*\rangle_0{}^2}{E_{\mathrm{n}\pi^*,\mathrm{n}\sigma^*}{}^2} \langle \mathrm{n}|m_y|\sigma^*\rangle_0 \langle \pi^*|m_x|\sigma^*\rangle_0 \Big\} \\ & \times \langle Q_r{}^2\rangle \end{aligned} \tag{6a}$$

or

$$\begin{aligned} B_r{}^0 \cong 4\,\mathrm{Im}\Big\{ & E_{\mathrm{n}\pi^*,\mathrm{A}}{}^{-1} \langle \mathrm{n}|\mu_z|\pi^*\rangle_0 \\ & \times \frac{\langle \sigma|H_r{}^{(1)}(\mathrm{b}_2)|\mathrm{n}\rangle_0{}^2}{E_{\mathrm{n}\pi^*,\sigma\pi^*}{}^2} \langle \sigma|m_x|\pi^*\rangle_0 \langle \mathrm{n}|m_y|\sigma\rangle_0 \Big\} \langle Q_r{}^2\rangle \end{aligned} \tag{6b}$$

for b_1 and b_2 modes, respectively. In formaldehyde, the important b_1 and b_2 modes are the out-of-plane bending mode (ν_4) and the antisymmetric C–H stretch (ν_5), respectively.

(C) **Development of a Stereochemical Model. (1) Some Numerical Considerations.** In this section, we use the equations of the previous one in conjunction with a CNDO/2 formalism described in the Applications B.2. In particular, it is shown that B values calculated by the GP method[10] (see eq 1) for rotamers of acetone can be mimicked by simpler CNDO/2 calculations using eq 6. This leads to the development of simple, parameterizable expressions (eq 18, 19, and 20) for approximating the B^V + B^{VS} terms which are associated with the substituents at the α carbons in saturated ketones.

As will later be confirmed by a comparison of calculated and experimental B values, one of the most important structural features is the orientation and type of α substituent. The orientation of an α substituent atom R is specified by the dihedral angle (ϵ) between the C–C_α–R plane and the C_α–C–O plane (Figure 1). The angle ϵ is zero when R is in the chromophoric plane and is closest to the oxygen atom (e.g., for α-equatorial substituents in cyclohexanone chairs $\epsilon < 15°$). Acetone is chosen as the prototypical ketone. Individual rotamers are denoted by specifying the smallest dihedral angle δ for each methyl group, so that the extended C_{2v} geometry of acetone is specified by $\delta_1 = 0$, $\delta_2 = 0$.

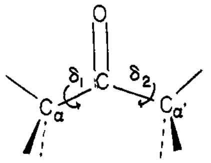


Table I. GP B_4 Values[a] from Rotamers of Acetone[b]

δ, deg	$B_4(Q) \times 10^8$	$B_4(-Q) \times 10^8$	A. B_4 Values $B(0) \times 10^8$	$[B_4(Q) + B_4(-Q)] \times 10^8/2$	$B_4 \times 10^8$
0	30	30	0	30	30
10	−45	118	1	36.5	35.5
20	−87	195	3	54	51
30	−90	241	1	75.5	74.5
40	−52	238	−7	93	100
50	18	188	−17	103	120
60	106	106	−22	106	128

δ, deg	$B_4{}^0(Q) \times 10^8$	$B_4{}^0(-Q) \times 10^8$	B. $B_4{}^0$ Values $B^0(0) \times 10^8$	$[B_4{}^0(Q) + B_4{}^0(-Q)] \times 10^8/2$	$B_4{}^0 \times 10^8$
0	43	43	0	43	43
10	14	73	−1	43.5	44.5
20	−7	97	vl−5	45	50
30	−13	106	−10	46.5	56.5
40	−4	101	−16	48.5	64.5
50	19	80	−20	49.5	69.5
60	51	51	−21	51	72

[a] The units for B values are $(\mu_B\, D^2)/\mathrm{cm}^{-1}$. [b] One methyl group is as in the extended C_{2v} rotamer, the other is rotated about the C–C$_\alpha$ axis by δ ($\delta_1 = 0$, $\delta_2 = \delta$).

Table II. One-Electron Matrix Elements[a] for Acetone Rotamers[b]

δ, deg	$\langle n\|m_y\|\sigma^*\rangle_0$	$\langle \pi^*\|m_x\|\sigma^*\rangle_0$	$\langle \sigma\|m_x\|\pi^*\rangle_0$	$\langle n\|m_y\|\sigma\rangle_0$
0	0.3756	−0.1144	0.2583	−0.2172
10	0.3749	−0.1232	0.2439	−0.2170
20	0.3728	−0.1473	0.2052	−0.2167
30	0.3699	−0.1802	0.1539	−0.2164
40	0.3669	−0.2132	0.1042	−0.2164
50	0.3646	−0.2374	0.0689	−0.2165
60	0.3637	−0.2463	0.0562	−0.2166

[a] Matrix elements are in atomic units (ea$_0$). [b] One methyl group as in the extended C_{2v} rotamer, the other rotated about the C–C$_\alpha$ axis by δ ($\delta_1 = 0$, $\delta_2 = \delta$).

The lowest order terms which contribute to B_r are quadratic in Q_r.[2a] Hence it is necessary in GP calculations to eliminate terms which are linear in the normal coordinates Q_r. The *vibrational* contribution of the mode Q_r to the total B value is therefore given in the GP method by

$$B_r = \tfrac{1}{2}[B_r(Q_r) + B_r(-Q_r)] - B(0) \qquad (7)$$

The arithmetic averaging in eq 7 eliminates the unwanted linear terms, and $B(0)$, the purely static contribution, the B^S term of eq 22, ref 2a, is subtracted off. Hence eq 7 corresponds to $B_r{}^V + B_r{}^{VS}$. Each of the B values in eq 7 is given in Table I, as are analogous values for $B_r{}^0$, for the out-of-plane bending motion in acetone.[17] This mode is the analogue of the ν_4 mode in formaldehyde; hence we denote the B_r value as B_4. Both B_4 and $B_4{}^0$ show significant changes with the rotation angle δ. As one methyl group is rotated (δ_1 goes from 0 to 60°, $\delta_2 = 0$), B_4 approximately quadruples and $B_4{}^0$ doubles.

In order to analyze the variations in B_4 and $B_4{}^0$ with δ, we first note that while $B_4{}^0$ is not as dominant as it was in formaldehyde,[10] it varies in the same general way with δ as B_4. Hence we may concentrate on $B_4{}^0$. In particular, we focus on the transition moments in eq 6a. These moments are given in Table II, as are the analogous moments from eq 6b for the b$_2$ antisymmetric stretch. Of all these factors, only $\langle\sigma^*|m_x|\pi^*\rangle_0$, which scales $B_4{}^0$, and $\langle\sigma|m_x|\pi^*\rangle_0$, which scales the negatively signed[9,10] B_{b_2} for the antisymmetric stretch, undergo significant changes with δ. For reasons which will become clear, we defer further consideration of $\langle\sigma|m_x|\pi^*\rangle_0$ and B_{b_2} until the end of this section.

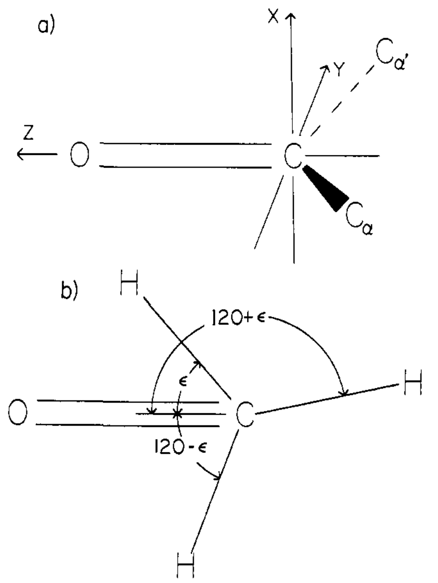


Figure 1. (a) Axis convention for the carbonyl chromophore. (b) Dihedral angles for the hydrogen atoms in one methyl group of acetone as viewed down the C–C$_\alpha$ bond. The methyl group is rotated by δ (=ϵ for $\epsilon \leq 60°$) degrees from the extended geometry. Tetrahedral hybridization at the C$_\alpha$ atom is assumed, so that the dihedral angles are ϵ, 120 + ϵ, and 120 − ϵ for $\epsilon \leq 60°$.

In Figure 2a are plots of $\langle\sigma^*|m_x|\pi^*\rangle_0$, in arbitrary units, and B_4 and $B_4{}^0$ vs. δ. A close correlation among $\langle\sigma^*|m_x|\pi^*\rangle_0$,

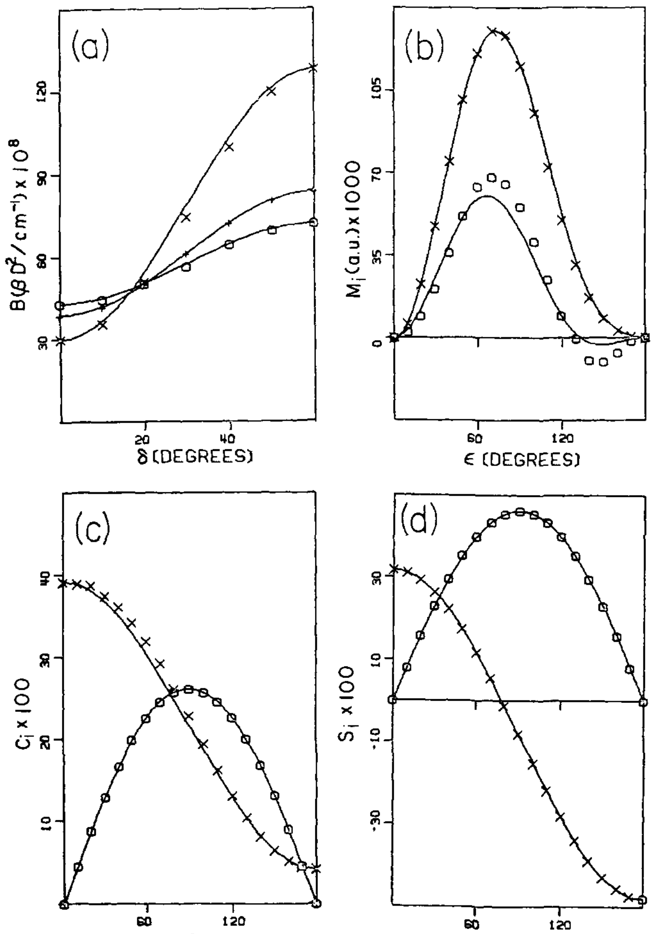


Figure 2. (a) GP B values of acetone [B_4 (×) and $B_4{}^0$ (□)] and $-339.4\langle\sigma^*|m_x|\pi^*\rangle_0$ (+) as functions of the methyl rotation angle δ. The fitted forms (solid lines) are (sums are over all hydrogen atoms) $B_4 = \Sigma_i\ (42.67 + 65.33 \cos \epsilon_i) \sin^2 \epsilon_i$, $B_4{}^0 = \Sigma_i\ (24.00 + 19.33 \cos \epsilon_i) \sin^2 \epsilon_i$, and $-339.4\langle\sigma^*|m_x|\pi^*\rangle = \Sigma_i\ (27.87 + 29.85 \cos \epsilon_i) \sin^2 \epsilon_i$. (b) Contributions, by atom, to the diagonal portion of $\langle\sigma^*|m_x|\pi^*\rangle$ [m_i, see text] for the hydrogen atoms in acetone (×) and the methyl carbon atoms in 3,3-dimethyl-2-butanone (□) as functions of the dihedral angle ϵ. Solid curves are m_i (×) = $(0.115 + 0.091 \cos \epsilon) \sin^2 \epsilon$ and m_i (□) = $(0.045 + 0.066 \cos \epsilon) \sin^2 \epsilon$. (c) Hydrogen 1s orbital coefficients in the σ^* (×) and π^* (□) orbitals of acetone as functions of ϵ. The solid lines are $C_{\sigma^*}{}^{\rm H} = (0.216 + 0.175 \cos \epsilon)$ and $C_{\pi^*}{}^{\rm H} = 0.261 \sin \epsilon$. (d) Overlaps of hydrogen 1s orbitals with the α-carbon $2p_z$ (×) and $2p_x$ (□) orbitals of acetone. The fitted lines are $S({\rm H,C}_{2p_z}) = (-0.081 + 0.399 \cos \epsilon)$ and $S({\rm H,C}_{2p_x})$ 0.461 $\sin \epsilon$.

B_4, and $B_4{}^0$ clearly exists, suggesting that much of the essential physics governing the variation of the B values with δ is contained in the variation of $\langle\sigma^*|m_x|\pi^*\rangle_0$.

We now expand $\langle\sigma^*|m_x|\pi^*\rangle_0$, and ignore two-center matrix elements of the electric dipole moment operator, **m**. Then $\langle\sigma^*|m_x|\pi^*\rangle_0$ may be written as

$$\langle\sigma^*|m_x|\pi^*\rangle_0 = \sum_A \left[\sum_i m_i + \sum_{\substack{i,j\\ i\neq j}} C_{\sigma^*}{}^i C_{\pi^*}{}^j \langle\phi_i|x|\phi_j\rangle\right] \tag{8}$$

where $m_i \equiv C_{\sigma^*}{}^i C_{\pi^*}{}^i X_A$, the C^i's are the coefficients of the ith AO (ϕ_i) in the indicated MO, X_A is the x coordinate (Figure 1) of the Ath nucleus, and the summations over i and j are over the AO's centered on the Ath nucleus. The summation of the m_i is referred to as the diagonal part of $\langle\sigma^*|m_x|\pi^*\rangle_0$ and the sum involving $\langle\phi_i|x|\phi_j\rangle$ is the polarizability term. The sums over specific atoms are given in Table IIIa, and it is clear that only the diagonal term involving the rotated hydrogen atoms shows a significant variation with δ. We therefore continue to investigate this part of $\langle\sigma^*|m_x|\pi^*\rangle_0$ and present the contributions of individual hydrogen atoms to it in Figure 2b. CNDO/2 calculations were also performed on 3,3-dimethyl-2-butanone in which the *tert*-butyl group was rotated around the C-C$_\alpha$ bond. The diagonal terms from the methyl carbon atoms which were rotated are also given in Figure 2b.

Evidently the variation of B_4 with δ is primarily due to variation of the m_i. The dependence of $C_{\sigma^*}{}^i$ and $C_{\pi^*}{}^i$ (eq 8), the MO coefficients which are associated with the rotated hydrogen atoms in acetone, upon the dihedral angle ϵ is illustrated in Figure 2c. In the CNDO approximations, matrix elements of the one-electron part of the Hamiltonian are proportional to the corresponding overlaps.[19,20] Accordingly, the overlaps between the hydrogen 1s AO's and the α-carbon AO's of interest (σ^* is largely an sp$_z$ hybrid at the α carbons, Table IIIb) are presented in Figure 2d. The agreement between the shapes of $C_{\pi^*}{}^i$ and $S({\rm H,C}_{2p_x})$ is extremely good; both may be expressed as a constant times $\sin \epsilon_i$ (Figures 2c and 2d). Also, $S({\rm H,C}_{2p_z})$ is given by $-0.0814 + 0.3989 \cos \epsilon_i$ (Figure 2d) and $S({\rm H,C}_{2s})$ is constant. The coefficient $C_{\sigma^*}{}^i$ may therefore be represented by $(k_1 + k_2 \cos \epsilon_i)$, where k_1 and k_2 are constants, and the agreement (Figure 2c) is excellent. As for the geometrical quantity X_i, it is equal to a constant times $\sin \epsilon_i$. The m_i should therefore be given by

$$m_i = (k_3 + k_4 \cos \epsilon_i) \sin^2 \epsilon_i \tag{9}$$

where k_3 and k_4 are constants. The agreement of this functional form with the calculated m_i in Figure 2b is quite good. Finally, the vibructional B values in Figure 2a are then representable as

$$B_4 \approx \sum_i^{\alpha} (a_i + b_i \cos \epsilon_i) \sin^2 \epsilon_i \tag{10}$$

where $\Sigma_i{}^\alpha$ means summation over all α substituents. Comparison of this functional form with *both* $B_4{}^0$ and B_4 (Figure 2a) indicates that eq 10 is a good approximation.

The above results suggest the following simplified perturbation model:

(i) Basis Set. Since variations in the orientations of the α substituents have been shown to affect the B terms significantly, we must include all valence AO's which are centered on the α carbons as well as those of the oxygen and carbonyl carbon atoms. We refer to this entire set as the α AO's. In addition, we include AO's which are centered on the α-substituent atoms and are either undirected (s orbitals) or are directed toward the α carbons (sp^3 hybrids). These atomic orbitals we denote as the β AO's.

(ii) Hamiltonian. The perturbation (H_α) associated with substitution at the α carbon in the one-electron model is that portion of the total Hamiltonian (H) which mixes the α and β AO's. We assume H_α to be proportional to overlap:

$$\begin{aligned}\langle\alpha|H_\alpha|\beta\rangle &= \kappa S(\alpha,\beta)\\ \langle\alpha|H - H_\alpha|\beta\rangle &= 0\end{aligned} \tag{11}$$

where κ is some constant. The perturbed σ^* and π^* MO's then are

$$\sigma^* \approx \sigma_0{}^* + \sum_i \kappa_i \langle\sigma_0{}^*|\beta_i\rangle\beta_i$$

$$\pi^* \approx \pi_0{}^* + \sum_i \kappa_i{}' \langle\pi_0{}^*|\beta_i\rangle\beta_i \tag{12}$$

where $\sigma_0{}^*$ and $\pi_0{}^*$ are eigenfunctions of $H - H_\alpha$ and κ_i and $\kappa_i{}'$ are constants. If we ignore two-center terms, as well as $\langle {\rm s}|\mathbf{m}|{\rm p}\rangle$ terms which involve the β AO's, the matrix element of interest becomes

$$\langle\sigma^*|m_x|\pi^*\rangle = \langle\sigma_0{}^*|m_x|\pi_0{}^*\rangle + \sum_i \kappa_i\kappa_i{}'\langle\sigma_0{}^*|\beta_i\rangle\langle\pi_0{}^*|\beta_i\rangle X_i \tag{13}$$

Table III

(a) Atomic Contributions[a] to $\langle \pi^* | m_x | \sigma^* \rangle_0$ in Acetone Rotamers[b]

Rotation Angle δ, deg	Diagonal terms[c]		Polarizability terms[d]				Total
	H_2,H_3[b]	H_4,H_5,H_6[b]	O	C	C_1	C_2	
0	−0.1002	−0.1002	0.0053	0.1892	−0.0542	−0.0542	−0.1144
10	−0.0996	−0.1097	0.0052	0.1892	−0.0541	−0.0543	−0.1232
20	−0.0982	−0.1356	0.0051	0.1893	−0.0536	−0.0543	−0.1472
30	−0.0963	−0.1709	0.0048	0.1893	−0.0529	−0.0543	−0.1803
40	−0.0945	−0.2061	0.0046	0.1893	−0.0522	−0.0542	−0.2132
50	−0.0932	−0.2321	0.0045	0.1893	−0.0518	−0.0541	−0.2374
60	−0.0929	−0.2415	0.0044	0.1893	−0.0516	−0.0540	−0.2463

(b) The CNDO/2 Coefficients of Certain Molecular Orbitals of Acetone[e] in its Extended (C_{2v}) Geometry

		π	σ	n	π^*	σ^*
2s	O	0	0.1198	0	0	−0.0143
	C	0	0.0229	0	0	0.3276
	C_1	0	0.0364	−0.1123	0	−0.4582
	C_2	0	0.0364	0.1123	0	−0.4582
$2p_x$	O	0.7229	0	0	−0.5798	0
	C	0.4352	0	0	0.6504	0
	C_1	−0.2246	0	0	0.1333	0
	C_2	−0.2246	0	0	0.1333	0
$2p_y$	O	0	0	0.7565	0	0
	C	0	0	−0.3255	0	0
	C_1	0	−0.0666	0.3302	0	−0.0271
	C_2	0	0.0666	0.3302	0	0.0271
$2p_x$	O	0	0.5795	0	0	0.0360
	C	0	−0.4075	0	0	−0.1597
	C_1	0	0.3499	−0.1601	0	−0.1886
	C_2	0	0.3499	0.1601	0	−0.1886
1s	H_1	0	0.2139	0.1032	0	0.3899
	H_2	−0.2163	−0.1840	0.0382	−0.2265	0.1315
	H_3	0.2163	−0.1840	0.0382	0.2265	0.1315
	H_4	0	0.2139	−0.1032	0	0.3899
	H_5	−0.2163	−0.1840	−0.0382	−0.2265	0.1315
	H_6	0.2163	−0.1840	−0.0382	0.2265	0.1315

[a] Units are ea_0. [b] The $C_1H_1H_2H_3$ methyl is held with H_1 in the carbonyl plane and directed toward the oxygen atom, and the $C_2H_4H_5H_6$ methyl group is rotated from the corresponding position by δ ($\delta_1 = 0$, $\delta_2 = \delta$). [c] Diagonal AO matrix elements m_i, see text. [d] Terms involving $\langle s | m_x | p_x \rangle$, see text. [e] These orbitals are the highest occupied or lowest virtual orbitals of the type specified.

where X_i is the x coordinate of the nucleus on which the AO β_i is centered. With the functional dependence previously determined for the overlaps, eq 13 becomes

$$\langle \sigma^* | m_x | \pi^* \rangle = \langle \sigma_0^* | m_x | \pi_0^* \rangle + \sum_i^{\alpha} (a_i' + b_i' \cos \epsilon_i) \sin^2 \epsilon_i \quad (14)$$

In eq 14, a_i' and b_i' depend upon the type of α substituent, and again Σ_i^{α} means summation over all α substituents. With the above assumptions, eq 6 becomes

$$B_r = B_0 + C_1^{\mathrm{H}} \sum_{\mathrm{H}}^{\alpha} \sin^2 \epsilon_{\mathrm{H}} + C_2^{\mathrm{H}} \sum_{\mathrm{H}}^{\alpha} \cos \epsilon_{\mathrm{H}} \sin^2 \epsilon_{\mathrm{H}} + C_1^{\mathrm{C}} \sum_{\mathrm{C}}^{\alpha} \sin^2 \epsilon_{\mathrm{C}} + C_2^{\mathrm{C}} \sum_{\mathrm{C}}^{\alpha} \cos \epsilon_{\mathrm{C}} \sin^2 \epsilon_{\mathrm{C}} \quad (15)$$

where C_1^{H} and C_2^{H} are appropriate constants for hydrogen substituents on the α carbons and similarly for C_1^{C} and C_2^{C} for carbon substituents. An a priori calculation of the constants which appear in eq 15 is unwarranted, but they can be evaluated from the experimental data.

(2) Some Discussion of Assumptions. Equation 15 has been developed on the basis of a number of rather extreme assumptions. This situation is mitigated somewhat by the fact that nongeometrical quantities appear as parameters that will ultimately be determined from experiment. However, one assumption does deserve special discussion.

The subscript 4 on B_4 serves as a remainder that eq 15 was derived from considerations of the out-of-plane bending mode only. Contributions of the b_2 antisymmetric stretch were neglected, although it was pointed out that via the matrix element $\langle \sigma | m_x | \pi^* \rangle_0$ they too vary with δ. We now note that an analysis similar to the one leading to eq 15 for B_4 gives precisely the same form for the antisymmetric stretch contribution to the MCD intensity. And since the nongeometrical quantities are evaluated empirically, the previous neglect of the antisymmetric stretch is without consequence.

That contributions from other modes may be cast in the same form as eq 15 is not immediately obvious. However, we shall make this assumption, or what has the same consequence, that these contributions are small. A defense of these latter assumptions can be made in part, but its value is somewhat moot in the context of the present work. We intend to use eq 15 and its equivalents to understand such apparent anomalies as two compounds which differ *structurally* only by a totally symmetric perturbation, but which exhibit widely disparate B values, e.g., cyclobutanone (**63**, $B(\mathrm{n}\pi^*, \mathbf{63}) = 158 \times 10^{-8}$) and 2,2,4,4-tetramethylcyclobutanone (**65**, $B(\mathrm{n}\pi^*, \mathbf{65}) = 82 \times 10^{-8}$). The ultimate justification for eq 15 will lie in its ability to provide insight into data such as those just cited.

Table IV. Geometrical Constants for Selected Example Compounds

Compd	$\Sigma_H \sin^2 \epsilon$	$\Sigma_H \cos \epsilon \sin^2 \epsilon$	$\Sigma_C \sin^2 \epsilon$	$\Sigma_C \cos \epsilon \sin^2 \epsilon$
Acetone (**42**)	3.00	−1.50	0.00	0.00
2,2,4,4-Tetramethyl-3-pentanone (**51**)	0.00	0.00	3.00	−1.50
Adamantanone (**21**)	0.00	0.00	2.87	−1.52
Cyclohexanone (**23**)	1.83	−0.54	1.17	−0.75
2(eq)-Methylcyclohexanone (**24**)	1.78	−0.58	1.20	−0.73
2(ax)-Methylcyclohexanone	0.95	−0.23	2.06	−1.05
Bicyclo[2.2.2]octan-2-one (**12**)	1.52	0.75	1.42	−0.76
3,3-Dimethylbicyclo[2.2.2]octan-2-one (**15**)	0.00	0.00	2.96	−0.06
Cyclopentanone (**52**)	2.98	1.29	0.08	−0.08
1,1,3,3-Tetramethyl-*cis*-2-hydrindanone (**61**)	0.00	0.00	3.03	1.25
Homocubanone (**59**)	0.00	0.00	1.99	−1.41
Cyclobutanone (**63**)	3.00	1.50	0.00	0.00
2,2,4,4-Tetramethylcyclobutanone (**65**)	0.00	0.00	3.00	1.50

Table V. GP B_4 Values for Acetone[a] as a Function of the C_α–C–$C_{\alpha'}$ Bond Angle (θ)[b]

θ, deg	$B_4 \times 10^8$ [c]	θ, deg	$B_4 \times 10^8$ [c]
135	135	105	166
127.5	157	100	(154)[d]
120	172	95	(138)[d]
112.5	176	90	(114)[d]

[a] Both methyl groups are rotated by 60° from the extended C_{2v} geometry (δ_1 = 60°, δ_2 = 60°). [b] For comparison, the B_4 value for cyclobutanone (θ = 90.6°) is 145×10^{-8}. [c] B values are given in units of $(\mu_B D^2)/cm^{-1}$. [d] These values are estimated by quadratic interpolation of the first five points.

In view of the above discussion, eq 15 amounts to an approximate expression for the $(B^V + B^{VS})$ terms of eq 22, ref 2a, for a model prototypical ketone composed of the carbonyl group and its α substituents. We will use the symbol $\overline{B}$ to denote this sum, i.e., $\overline{B} = (B^V + B^{VS})$.

(3) Model Expressions. We shall use eq 15 to help interpret the variation of MCD intensity with variation in the stereochemistry of the α substituents. Before doing so, however, we put eq 15 in a slightly more convenient form.

Equation 15 may be written as

$$\overline{B} = B_0 + (C_1{}^H - C_1{}^C) \sum_H^\alpha \sin^2 \epsilon_H + C_2{}^H \sum_H^\alpha \cos \epsilon_H \sin^2 \epsilon_H + C_1{}^C\left(\sum_H^\alpha \sin^2 \epsilon_H + \sum_C^\alpha \sin^2 \epsilon_C\right) + C_2{}^C \sum_C^\alpha \cos \epsilon_C \sin^2 \epsilon_C \quad (16)$$

The trigonometric identity

$$\sin^2 \epsilon + \sin^2 (120° + \epsilon) + \sin^2 (120° - \epsilon) = 1.5 \quad (17)$$

shows that the fourth term in eq 16 is approximately constant (it is exactly so for tetrahedral coordination at the α carbons) and it is therefore very probably indistinguishable from B_0. Hence we combine these terms and write eq 16 as

$$\overline{B} = K_1{}^H \sum_H^\alpha \sin^2 \epsilon_H + K_2{}^H \sum_H^\alpha \cos \epsilon_H \sin^2 \epsilon_H + K_1{}^C \sum_C^\alpha \sin^2 \epsilon_C + K_2{}^C \sum_C^\alpha \cos \epsilon_C \sin^2 \epsilon_C \quad (18)$$

where $K_1{}^H$, $K_2{}^C$, etc., are constants analogous to those in eq 15. Representative values of the geometrical factors which appear in eq 18 are given in Table IV.

An assumption implicit in the derivation of eq 15 is that the only geometrical parameters which vary are the types and orientations of the α substituents. However, another structural parameter of interest is the C_α–C–$C_{\alpha'}$ angle, θ. The GP calculations for B_4 for acetone as a function of θ (Table V) show that B_4 varies appreciably with θ. (In cyclohexanone,[21] $\theta \sim$ 116°; in cyclopentanone,[22] $\theta \sim$ 110°; in cyclobutanone,[23] $\theta \sim$ 90°.) Thus although eq 16 or 18 may be applied to cyclohexanones, cyclopentanones, or cyclobutanones, a different set of values for the nongeometrical constants is necessary in each case. An attempted analysis of these bond angle effects was not too informative, largely because all the transition moments in eq 6 are strong functions of θ.

Since the dihedral angles for all α substituents are the same in the cyclobutanones, eq 18 takes the linear form

$$\overline{B}(\text{cyclobutanones}) = n_H\beta + \beta_0 \quad (19)$$

where n_H is the number of α hydrogens, and β and β_0 are constants to be determined from the data. Equation 19 holds in other series as well, provided that the constants are suitably redefined. For instance, for the extended conformation of acyclic ketones, we may write

$$\overline{B}(\text{acyclic ketones}) = n_H\beta' + \beta_0' \quad (20)$$

where n_H is the number of α hydrogens which are out of the chromophoric plane.

Applications

(A) Preliminary Remarks. The original protocol for analyzing the variations in MCD intensity in ketones is given in ref 9. It is shown there that by use of simple projection diagrams, structural perturbations may be classified according to the nontotally symmetric irreducible representations (A_2, B_1, B_2) of C_{2v}, and also that signs may be associated with them (see eq 13, ref 9).[24] Hence, by examining the frequency of nontotally symmetric structural perturbations of different kinds, the observed variations in experimental B values could be understood, at least qualitatively, when appropriate considerations were made for vibrational contributions to the MCD. Except for conformational stabilization effects (see Theory B.3.e, ref 9) totally symmetric structural perturbations were ignored since only nontotally symmetric perturbations can generate MCD intensity. In the language of the present paper, we worried about B^S terms, and in part about B^V terms, but had neglected other B^V and B^{VS} terms, i.e., the effect of vibructions. We now apply eq 18, 19, and 20 and show that taking cognizance of these terms adds considerably to our understanding of MCD data–structural relationships.

(B) Geometries and Computer Programs. (1) Geometries. For the substituted cyclohexanones, cyclopentanones, and cyclobutanones, we used idealized geometries.[23,25,26] The geometry of the ring containing the keto group in the *trans*-2-decalones is taken to be the same as that of the corresponding chair cy-

Table VI. B Values for Selected Saturated Ketones[a]

	Compd[b]	$B(n\pi^*) \times 10^8$
1	*trans*-2-Decalone	29
2	1(eq)-Methyl-*trans*-2-decalone[c]	−5
3	3(eq)-Methyl-*trans*-2-decalone[d]	35
4	1(eq),3(eq)-Dimethyl-*trans*-2-decalone[d]	27
5	1(ax)-Methyl-*trans*-2-decalone[d]	0
6	3(ax)-Methyl-*trans*-2-decalone[d]	−46
7	1,1-Dimethyl-*trans*-2-decalone[d]	−28
8	1,1,3(eq)-Trimethyl-*trans*-2-decalone[d]	−12
9	8,8,10-Trimethyl-*trans*-2-decalone[e]	38
10	5(eq),10-Dimethyl-*trans*-2-decalone[f]	22
11	5,5,9(ax)-Trimethyl-*trans*-2-decalone[e]	30
12	Bicyclo[2.2.2]octan-2-one[d]	73
13	1-Methylbicyclo[2.2.2]octan-2-one[d]	73
14	3-Methylbicyclo[2.2.2]octan-2-one[d]	66
15	3,3-Dimethylbicyclo[2.2.2]octan-2-one[d]	−10
16	4-Methylbicyclo[2.2.2]octan-2-one[d]	47
17	5(*endo*)-Methylbicyclo[2.2.2]octan-2-one[d]	70
18	6(*endo*)-Methylbicyclo[2.2.2]octan-2-one[d]	86
19	*trans*-1-Decalone	−4
20	Tricyclo[2.2.2.2]decan-2-one[g] (twistanone)	−28
21	Adamantan-2-one	−21
22	Bicyclo[3.3.1]nonan-2-one	−13
23	Cyclohexanone	6
24	2-Methylcyclohexanone	2
25	3-Methylcyclohexanone	27
26	4-Methylcyclohexanone	30
27	*cis*-2,6-Dimethylcyclohexanone	−8
28	*trans*-2,6-Dimethylcyclohexanone[h]	−16
29	3,3,5-Trimethylcyclohexanone	11
30	2,2-Dimethylcyclohexanone[i]	−17
31	3,3,5,5-Tetramethylcyclohexanone	24
32	2,2,6,6-Tetramethylcyclohexanone[j]	−176
33	2,2,6,6-Tetraethylcyclohexanone[j]	−106
34	2-*tert*-Butylcyclohexanone	10
35	3-*tert*-Butylcyclohexanone	53
36	4-*tert*-Butylcyclohexanone	−10
37	*cis*-2,6-Di-*tert*-butylcyclohexanone	6
38	*trans*-2,6-Di-*tert*-butylcyclohexanone	−9
39	*cis*-3,5-Di-*tert*-butylcyclohexanone	193
40	4-Ethylcyclohexanone	7
41	4-Isopropylcyclohexanone	4
42	2-Propanone	46
43	2-Butanone	44
44	3-Methyl-2-butanone	14
45	3,3-Dimethyl-2-butanone	−17
46	3-Pentanone	19
47	2-Methyl-3-pentanone	0
48	2,2-Dimethyl-3-pentanone	−20
49	2,4-Dimethyl-3-pentanone	25
50	2,2,4-Trimethyl-3-pentanone	−47
51	2,2,4,4-Tetramethyl-3-pentanone	−70
52	Cyclopentanone	95
53	3-Methylcyclopentanone	109
54	*trans*-2,3-Dimethylcyclopentanone	79
55	*cis*-3,4-Dimethylcyclopentanone	106
56	*trans*-3,4-Dimethylcyclopentanone	103
57	2,2,4,4-Tetramethylcyclopentanone	15
58	*cis*-2-Hydrindanone	120
59	Homocubanone[k]	29
60	Homocuneone[l]	26
61	1,1,3,3-Tetramethyl-*cis*-2-hydrindanone[m]	−20
62	Bicyclo[2.2.1]heptan-2-one (norbornanone)	19
63	Cyclobutanone	158
64	3,3-Dimethylcyclobutanone[m]	121
65	2,2,4,4-Tetramethylcyclobutanone[m]	82
66	2,2-Dimethylcyclobutanone[n]	102
67	*cis*-2,4-Dimethylcyclobutanone[m]	156
68	*trans*-2,4-Dimethylcyclobutanone[m]	129
69	*cis*-2,4-Diisopropylcyclobutanone[m]	125
70	*trans*-2,4-Diisopropylcyclobutanone[m]	148
71	*cis*-2,4-Di-*tert*-butylcyclobutanone[m]	179
72	*trans*-2,4-Di-*tert*-butylcyclopentanone[m]	176

[a] Spectrograde cyclohexane. B values are in units of $(\mu_B D^2)/\mathrm{cm}^{-1}$. [b] Data taken from ref 9 except as given in Applications C or as noted. [c] G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuzt, *J. Am. Chem. Soc.* **87**, 275 (1965). [d] K. Morrill, R. E. Linder, E. M. Bruckmann, G. Barth, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *Tetrahedron*, in press. [e] G. Ohloff, F. Näf, R. Decorzant, W. Thommen, and E. Sundt, *Helv. Chim. Acta*, **56**, 1414 (1973). [f] E. Piers and M. B. Geraghty, *Can. J. Chem.* **51**, 2166 (1973). [g] J. Hudec, private communication. [h] F. S. Johnson, *Chem. Commun.*, 1448 (1969). [i] L. Hub, private communication. [j] J. E. Stan and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966). [k] W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966). [l] W. G. Dauben and R. J. Twieg, *ibid.*, 531 (1974). [m] S. Dixon, R. E. Linder, G. Barth, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *Spectrosc. Lett.*, in press. [n] M. Kielczewski, private communication.

clohexanone ring.[25] The acyclic ketones are taken to be in the extended, or zigzag, conformation. Support for this assumption is provided by the work of Buric and Krueger,[27] who showed that diethyl ketone exists primarily in the trans, as opposed to the gauche, conformation (ΔH = 1.3 kcal/mol). (While there is undoubtedly torsional motion about the C–C_α bonds in this series, quantitation is difficult. For qualitative implications of such motion see Applications D.1.c.) The assumed bond lengths in the acyclics are C=O, 1.22 Å; C–C_α, 1.52 Å; C_α–H, 1.09 Å. The C_α–C–$C_{\alpha'}$ bond angle is taken to be 120°, and the C_α–C–H and C_α–C–C bond angles are assumed to be tetrahedral. For the bicyclo[2.2.2]octan-2-ones, and other bridged compounds, a force field program written by Wipke[28] was used to generate geometries.

Force field calculations by Schäfer[29] on two of the axially substituted *trans*-2-decalones established that only the chair–chair conformation is significantly populated in these compounds. Hence this was the conformation used.

(2) **Computer Programs.** The CNDO/2 calculations were performed using a slightly modified version of the program available from the Quantum Chemistry Program Exchange[30] as QCPE 91 and the modifications were cross checked using QCPE 141. The approximations made in the GP calculations were as previously given.[10] The multiple linear regression program BMDO2R[31] was used to evaluate the nongeometrical constants in eq 18.

(C) **Experimental.** The magnetic circular dichrometer and usual experimental procedures are described elsewhere,[8,9] as are the detailed spectral data[9] for several of the compounds listed in Table VI.

The synthetic procedures used in obtaining some *trans*-2-decalones (**3–8**), bicyclo[2.2.2]octan-2-ones (**12–18**), and cyclobutanones (**64–72**) are described in ref 13 and 14. All samples obtained commercially (**29, 31, 42–51,** Chemical Samples Co., Columbus, Ohio; **41,** Frinton Laboratories, S. Vineland, N.J.) were checked for purity by analytical gas chromatography and further purified by preparative gas chromatography as required.

(D) **Comparisons with Experiment. (1) Comparisons within Classes. (a) *trans*-2-Decalones.** The MCD spectra of a series of methyl-substituted *trans*-2-decalones (**2–11**) are presented in Figures 3–5. In each figure, the spectrum of the parent (**1**) is also shown for comparison. Figure 3 shows the spectra of decalones with equatorial α-methyl substituents (**2–4**), Figure

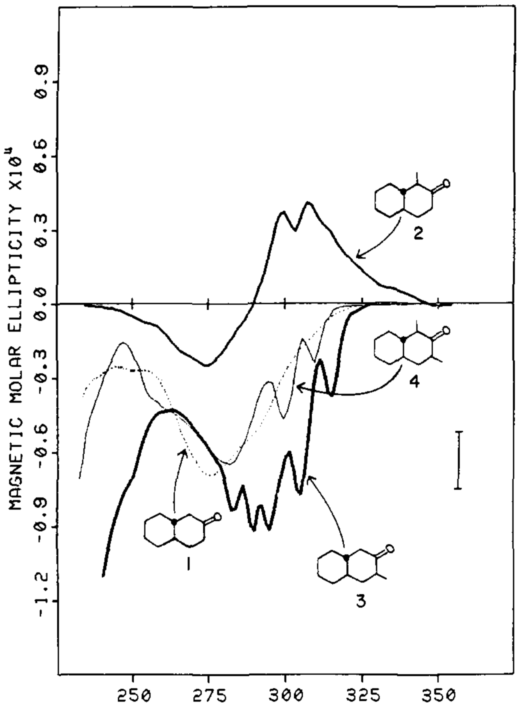


Figure 3. The MCD spectra of *trans*-2-decalone (1) and its α-(eq)-methyl derivatives (2–4).

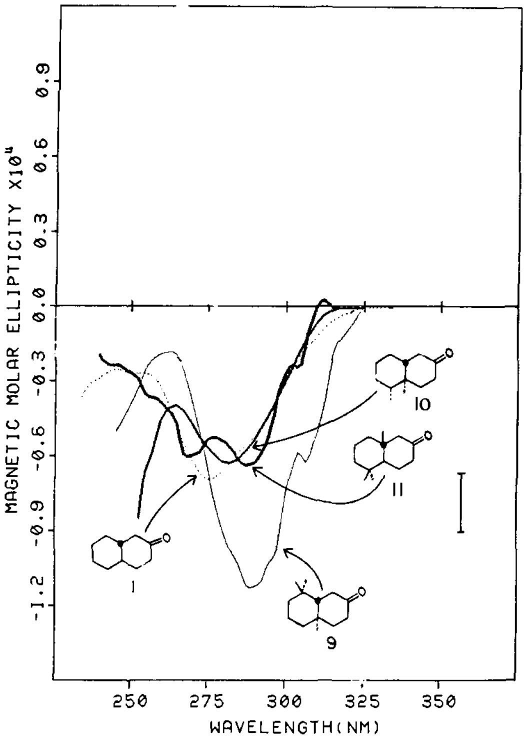


Figure 5. The MCD spectra of *trans*-2-decalone (1) and some β- and γ-methyl derivatives (9–11).

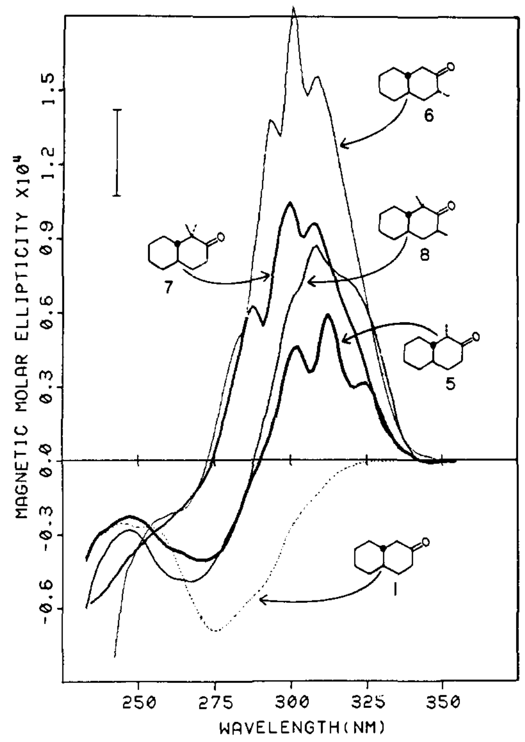


Figure 4. The MCD spectra of *trans*-2-decalone (1) and its α-(ax)-methyl derivatives (5–8).

4 shows those with axial α methyls (5–8), and Figure 5 shows those which are substituted at other than the α position (9–11). Generally, the compounds with an α-axial methyl group exhibit a clearly positive MCD component (negative B value) and those without show only negative MCD bands. The one exception to this statement is 1(eq)-methyl-*trans*-2-decalone (2). However, examination of the projection diagrams shows that it should have an integrated MCD spectrum that is more positive than that of the parent *trans*-2-decalone, as is the case. The B values for this series (Table VI) reflect the relatively strong negative effect of α-axial methyl substitution. When an α-axial methyl is present, the average B value is -21×10^{-8}; when none is present, the average B value is $+25 \times 10^{-8}$.

The above data are consonant with eq 18, which predicts a relatively large negative vibructional effect for α-axial methyl substitution. With the use of appropriate constants from Table VII, one calculates the vibructional effect to be $\bar{B} = -27 \times 10^{-8}$ for the idealized geometry.[25] On the other hand, for α-equatorial substitution, the vibructional effect is calculated from eq 18 to be only -3×10^{-8}. Indeed, the B values for 1(eq),3(eq)-dimethyl-*trans*-2-decalone (4) and *trans*-2-decalone, which should differ from each other essentially only by the vibructional effects of di-α-equatorial methyl substitution, are quite comparable ($B(n\pi^*,4) = 27 \times 10^{-8}$ and $B(n\pi^*,1) = 29 \times 10^{-8}$).

It follows from the discussion just given that the vibructional perturbations may be comparable in magnitude to the purely structural perturbations and hence should be taken into account when the methods of ref 9 are used to interpret MCD data. If one does so in detail, a number of apparent anomalies and previously surprisingly large changes in MCD intensity upon substitution can be understood. We hasten to add, however, that the present analysis does not resolve all such anomalies. For example, 3(ax)-methyl-*trans*-2-decalone (6) shows $B(n\pi^*,6) = -47 \times 10^{-8}$ compared to $B(n\pi^*,1) = +29 \times 10^{-8}$ for he parent *trans*-2-decalone (1). Even after account is taken of the negative contribution from the α-axial vibruction, the projection diagrams for (6) indicate that $B(n\pi^*,6)$ should have a significantly larger value than it does. It is possible here that distinct deviations from idealized geometry sufficient to explain the discrepancy occur, as they do in the case of 2,2,6,6-tetramethylcyclohexanone (32) (see Applications D.2, especially ref 37). However, no unequivocal independent evidence can be adduced for such an assertion, and the example is best classified as anomalous.[38]

Table VII. Statistical Results[a]

	θ, deg	N	σ	R	F	K_1^H	K_2^H	K_1^C	K_2^C
I	~116-120	44[b]	17.6	0.883	36	38.5	54.4	−2.4	27.0
II	~110	11[c]	20.2	0.978	39	42.1	−19.6	−3.6	−17.7
III	~110	11	19.0	0.978	58	33.4		−3.4	−17.2
IV	~110	11	18.6	0.976	90	33.0			−15.9

[a] The statistical results are calculated from the variables, not their deviations from their means.[31] Here θ is the approximate C_α–C–$C_{\alpha'}$ bond angle, σ is the standard error, R is the multiple correlation coefficient, F is the F value, and the K's are the nongeometrical constants of eq 18. [b] Preliminary calculations showed that the calculated B values of 2,2,6,6-tetramethylcyclohexanone (**32**) and 3,5-di-*tert*-butylcyclohexanone (**39**) deviated by more than three standard errors from the experimental values. Hence these and related compounds (**33, 35, 36, 40,** and **41**) were omitted. See ref 34 and 37 for a discussion. The data set here is then all of the other compounds listed in Table VI which are acyclic or which contain a cyclohexanone ring. [c] Because of the limited data set here, K_1^H and K_2^H are essentially completely correlated (0.998). This occurs because there is little variation in the α-hydrogen dihedral angles in the series so that K_1^H and K_2^H may not be determined separately here. Since K_1^C is found to be small, we may use the coefficients in any of calculations **II**, **III**, or **IV** to describe this data set.

Table VIII. Relative Intensities of the 655-cm^{-1} Raman Band in the 4-Substituted Cyclohexanones[a]

Compd	Rel int
Cyclohexanone	1.0
4-Methylcyclohexanone	0.65
4-Ethylcyclohexanone	0.53
4-Isopropylcyclohexanone	0.38
4-*tert*-Butylcyclohexanone	0.07

[a] Details of the experimental procedures will be given in the forthcoming Ph.D. Dissertation of one of us (K.M.).

(b) Cyclobutanones. Cyclobutanones have only one position (the three position) for other than α substitution. In addition, because all α substituents have identical out-of-plane angles ϵ, the vibruction equation (eq 19) is quite simple. In such circumstances, use of the vibruction terms in conjunction with the projection diagrams does produce a significant clarification of the data.

Figure 6 contains the MCD spectra of some representative cyclobutanones (**63–68**). For a more detailed comparison we turn to Figure 7. The upper solid line in Figure 7 is obtained by calibrating eq 19 with $B(\mathrm{n}\pi^*,\mathbf{63})$ (=158 × 10^{-8}) and $B(\mathrm{n}\pi^*,\mathbf{65})$ (=82 × 10^{-8}). All of the trans (C_2) and cis (C_s) derivatives (**67–72**) have B values that lie above the vibruction line (120 × 10^{-8} for α-dimethyl substitution), as they should; all members of the trans (C_2) series have only A_2 structural perturbations (Figure 8); all members of the cis (C_s) series have only B_1 structural perturbations; and both types of perturbations contribute positively to the B values (see eq 13, ref 9). The *gem*-dimethyl ($C_{s'}$) derivative (**66**) exhibits only a negative B_2 structural perturbation, and so should fall below the vibruction line, as it does.

The C_2 series (**68, 70, 72**) is quite regular, showing that the A_2 static contribution of a substituent group increases in the order Me < *i*-Pr < *t*-Bu. The B values of **68, 70,** and **72** are 129 × 10^{-8}, 148 × 10^{-8}, and 176 × 10^{-8}, respectively. The more crowded C_s series is less regular, $B(\mathrm{n}\pi^*,\mathbf{67}) = 156 \times 10^{-8}$, $B(\mathrm{n}\pi^*,\mathbf{69}) = 125 \times 10^{-8}$, and $B(\mathrm{n}\pi^*,\mathbf{71}) = 179 \times 10^{-8}$, and the crowding may be causing conformation stabilization to play a role here.

The only cyclobutanone not handled by the above protocols is 3,3-dimethylcyclobutanone (**64**) ($B(\mathrm{n}\pi^*,\mathbf{64}) = 121 \times 10^{-8}$). The B value here is significantly less than that of cyclobutanone (**63**) ($B(\mathrm{n}\pi^*,\mathbf{63}) = 158 \times 10^{-8}$), although the structural perturbation is A_1. These data serve to remind us of an important limitation of the vibrutional analysis we have given, in addition to those imposed by the stated assumptions. Our model for vibructions extends only to substituents at the α carbons, and as such can say nothing about vibructions associated with substitution at positions farther away from the carbonyl group. Compound **64** presents a case where the *only* perturbations are just such vibructions and hence lies outside our current analysis. Indeed, a closer look at the situation suggests the potential value of extending the model to encompass the other positions. More extensive CNDO/2 calculations (unpublished work) for cyclobutanones indicate that the H atoms at the 3-position have appreciable electron density in the π^* and in some σ^* orbitals, and hence substitution at this position might give rise to nontrivial vibructional contributions.

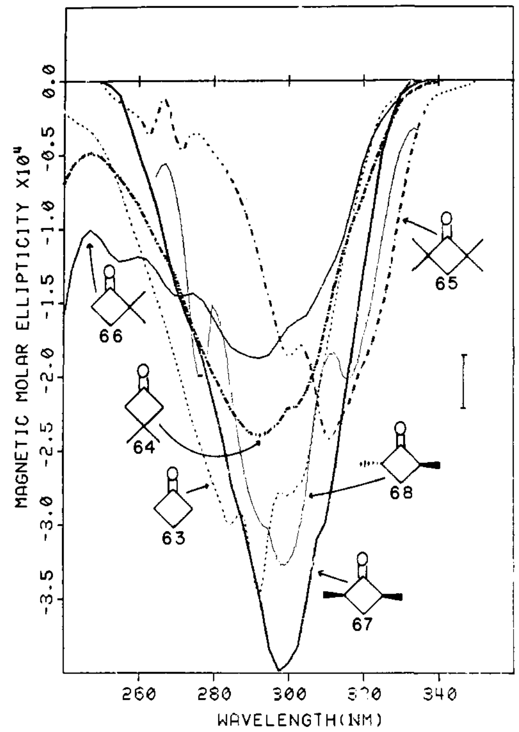


Figure 6. The MCD spectra of cyclobutanone (**63**), some of its dimethyl derivatives (**64, 66–68**), and 2,2,4,4-tetramethylcyclobutanone (**65**).

(c) Acyclic Ketones. The MCD spectra of some representative acyclic ketones, the R_2CO series (**42, 46, 49, 51**), are shown in Figure 9, and the B values for the entire series are given in Table VI. The effects of vibructions are evident in a general trend in the data: the more α substitution, the lower the B value. The average B values are 36 × 10^{-8} for no, 7 × 10^{-8} for one, 4 × 10^{-8} for two, −47 × 10^{-8} for three, and −71 × 10^{-8} for four out-of-plane α-methyl groups.

If one assumes the extended geometry for the acyclic ketones, and uses the B values for 3-pentanone (**46**) and 2,2,4,4-tetramethyl-3-pentanone (**51**) to obtain values for β_0' and β' in eq 20, one obtains the vibruction line shown in the

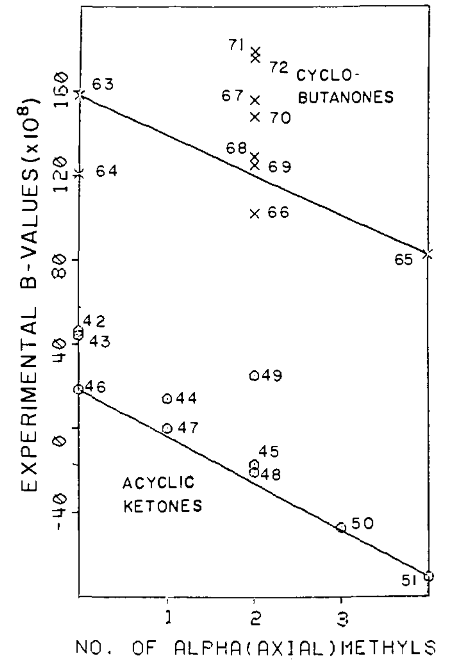


Figure 7. The experimental B values of the cyclobutanones and acyclics as a function of the number of out-of-plane α-methyl groups. The solid lines are the $\bar{B}$ values predicted by eq 19 and 20 when the B values for **63**, **65**, and **46**, **51** are used to evaluate the constants.

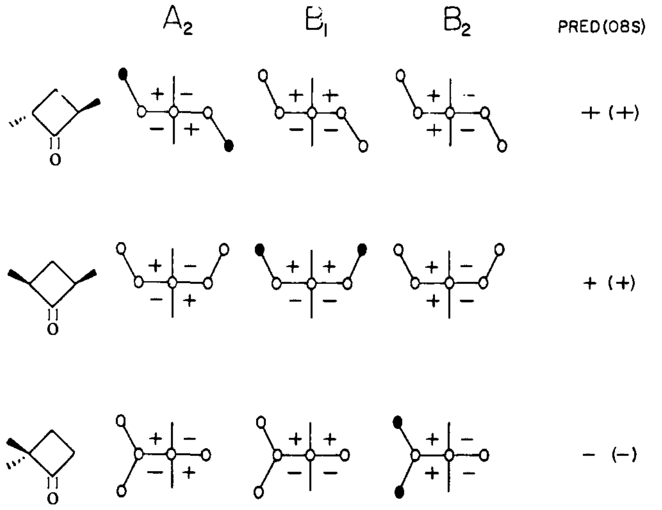


Figure 8. Projection diagrams for α,α or α,α' disubstituted cyclobutanones.

lower half of Figure 7. The B values for the entire series are shown there also.

Since the acyclic ketones present the possibility of a variety of rotomeric forms, there is no difficulty in rationalizing the data with arguments of high plausibility but perhaps of doubtful accuracy. Hence we limit ourselves here to just a few interpretive statements.

Calculations for acetone (**42**) and 3-pentanone (**46**) (see also Figure 2a and eq 18) show that conformers in which the α-hydrogens are out of the carbonyl plane and forward of the α-carbon make positive contributions to the B values. Since the torsional barrier[32] in acetone (**42**) is considerably less than it is in 3-pentanone (**46**), such rotomeric forms are more populous in **42**, and hence the higher B value of **42** as compared to **46** and similarly for **43** vs. **46**.

The largest deviation from the vibruction line is shown by 2,4-dimethyl-3-pentanone (**49**). Since the structural perturbation here is a strong A$_2$, this is quite understandable.

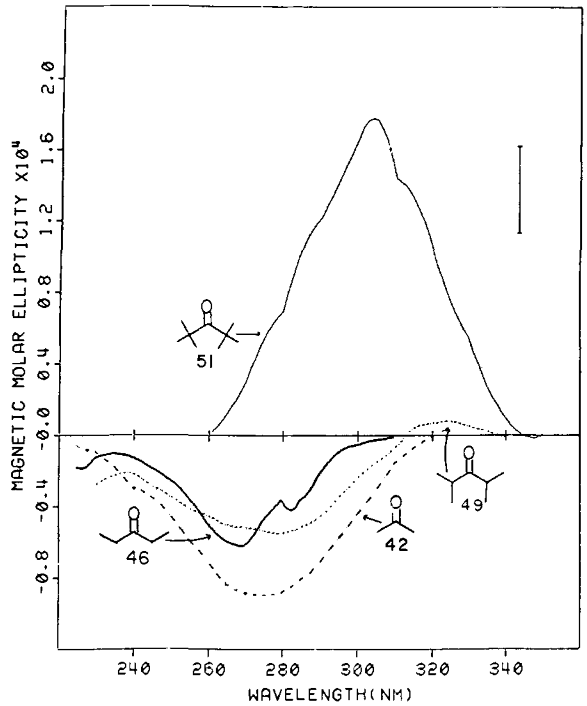


Figure 9. The MCD spectra of a series of symmetrically substituted acyclic ketones R_2CO (**42**, **46**, **49**, and **51**).

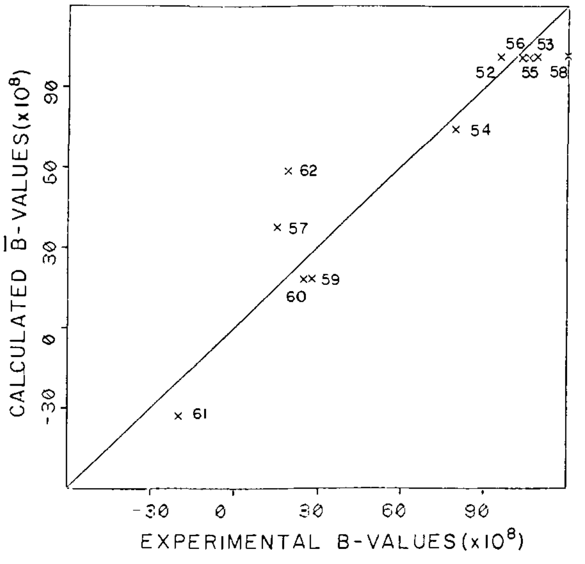


Figure 10. Results of a least-squares fit of eq 18 to the B values of the cyclopentanones (**52–62**).

(d) Cyclopentanones. The cyclopentanones provide an excellent example of the importance of vibructional effects. The relevant MCD data are given in Table VI (compounds **52–62**) and are plotted in Figure 10 against the $\bar{B}$ values calculated from eq 18.[33] (The nongeometrical constants for eq 18 are given in Table VII.)

Figure 10 is a somewhat different kind of vibructional plot than that given in Figure 7. In Figure 10 deviations from the 45° straight line are a measure of the structural contributions B^S. It will be noted that the points tend to follow the line over the entire range of B values (ca. -30×10^{-8} to ca. 120×10^{-8}), indicating the importance of the vibructional concept for an understanding of the data.

The somewhat wide range of B values exhibited by the cyclopentanones is related to the range of angles ϵ for substituents

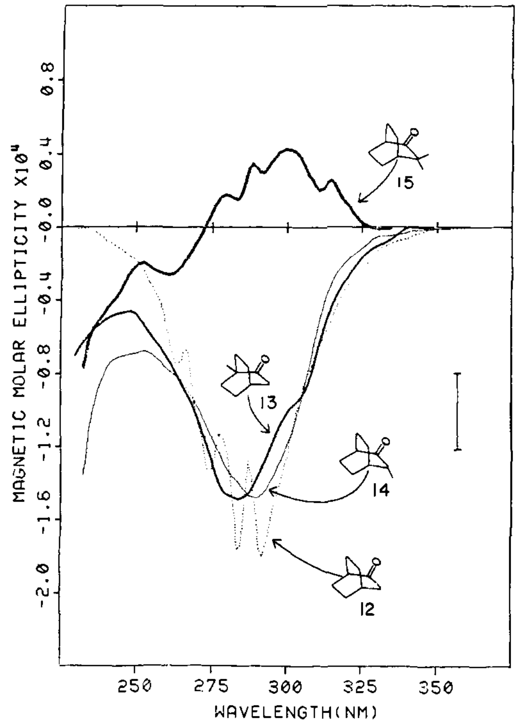


Figure 11. The MCD spectra of bicyclo[2.2.2]octan-2-one (**12**) and its α-methyl derivatives (**13–15**).

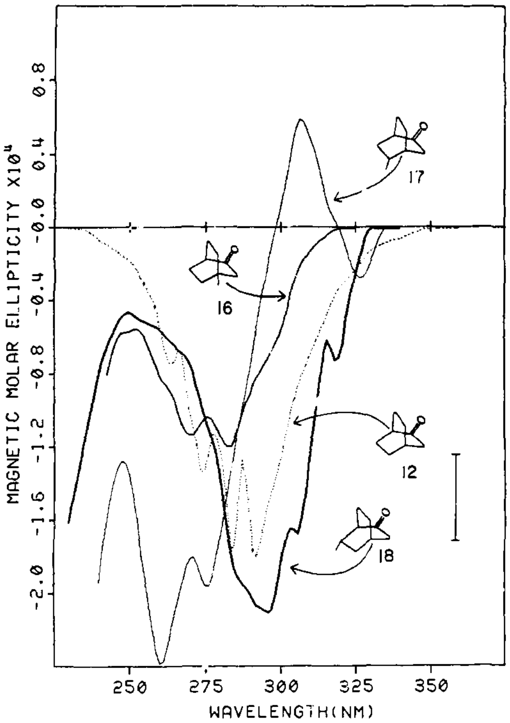
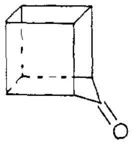


Figure 12. The MCD spectra of bicyclo[2.2.2]octan-2-one (**12**) and some β- and γ-methyl derivatives (**16–18**).

at the α-carbons. For example, in cyclopentanone (**52**) and 1,1,3,3-tetramethyl-*cis*-2-hydrindanone (**61**) the out-of-plane α substituents are directed "forward" toward the carbonyl oxygen ($\epsilon \sim 60°$), while in homocubanone (**59**) and homocuneone (**60**) they are directed "rearward", away from the carbonyl oxygen ($\epsilon \sim 130°$). We shall hereafter refer to such α substituents simply as being "forward" or "rearward", respectively.



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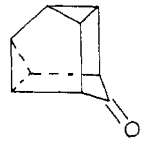
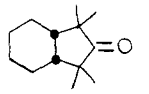


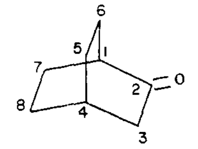
60



61

Forward and rearward α-substituent carbon atoms may and most frequently will make oppositely signed vibructional contributions in cyclopentanones. This behavior is related to the $\cos \epsilon \sin^2 \epsilon$ term in eq 18, which changes sign at $\epsilon = 90°$, and the relative values of the appropriate coefficients in entries II, III, and IV of Table VII. Moreover, these contributions may be relatively strong. Thus the large difference in B values between homocubanone ($B(n\pi^*,\mathbf{59}) = 29 \times 10^{-8}$) and 1,1,3,3-tetramethyl-*cis*-2-hydrindanone ($B(n\pi^*,\mathbf{61}) = -19 \times 10^{-8}$) is very much related to the fact that the α-substituent carbon atoms are rearward in **59** (positive B contribution) but are forward in **61** (negative B contribution). A distinction between forward and rearward α-substituents is also of importance in compounds containing cyclohexanone rings, e.g., see footnote 37.

(e) Bicyclooctanones. The MCD spectra of several substituted bicyclo[2.2.2]octan-2-ones (**12–18**) are shown in Figures 11 and 12. Figure 11 shows those with (**13–15**) and Figure 12 shows those without (**12** and **16–18**) α substituents. The large reduction in B value for 3,3-dimethylbicyclooctanone ($B(n\pi^*,\mathbf{15}) = -10 \times 10^{-8}$) from the value for the parent bicyclooctanone ($B(n\pi^*,\mathbf{12}) = 73 \times 10^{-8}$) again reflects the importance of vibructional effects associated with substitution of methyl groups for hydrogens at forward α-substituent positions. The reduction in B value for 3-methylbicyclo[2.2.2]octan-2-one ($B(n\pi^*,\mathbf{14}) = 66 \times 10^{-8}$) is less because of additional A_2 and B_1 structural perturbations that act counter to the vibructional effect, as can be seen from projection diagrams.



In attempting to apply the projection diagrams analysis o the bicyclooctanones, one serious anomaly arises in connection with 4-methylbicyclo[2.2.2]octan-2-one ($B(n\pi^*,\mathbf{16}) = 47 \times 10^{-8}$). Here the large reduction in B value compared to the parent compound **12** cannot be accounted for from the projection diagrams or our vibructional model. We do note, however, that the substitution again is at a position that lies outside the scope of our vibructional model (cf. compound **64** in Applications D.1.b).

(f) Cyclohexanones. The MCD spectra of a number of cyclohexanones (**23–41**) and an analysis of these have been presented previously.[9] The new points to be made in connection with these data are given in Applications D.2.

(2) Comparisons among Classes. The contents of Applications 1.D.a–e emphasized the importance of vibructions in providing an understanding of the variation in B values that can occur with structural changes within a single class of ketones. It is also of some interest to examine how vibructional effects enter into the skeletal changes that distinguish one class of ketones from another. For this purpose, we have made a vibructional plot (Figure 13) of virtually all of the ketones[34] in Table VI that may be assumed to have a C_α-C-$C_{\alpha'}$ angle θ of approximately 120°. The relevant nongeometrical constants for eq 18 from the regression analysis are given in Table VII. Again, deviations from the 45° straight line are a measure of the static structural contributions B^S.

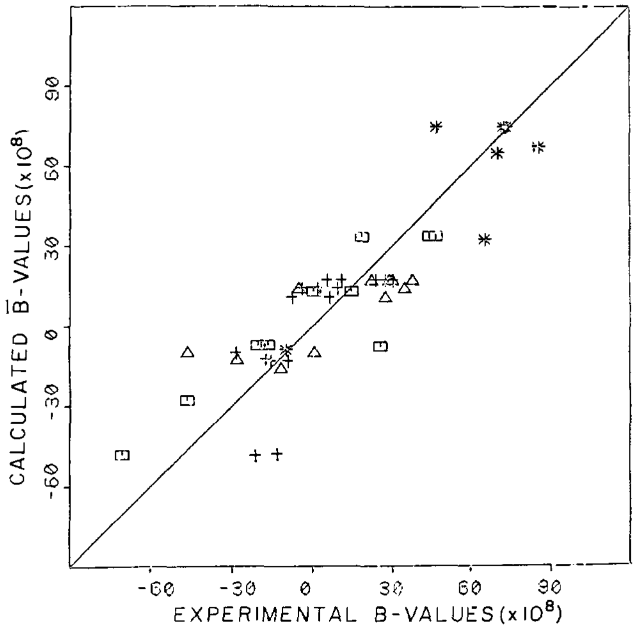


Figure 13. Results of a least-squares fit of eq 18 to the B values of ketones with a C_α-C-$C_{\alpha'}$ bond angle of about 120°: *trans*-2-decalones (△); cyclohexanones (+); bicyclo[2.2.2]octan-2-ones (*); acyclic ketones (⊡).

The range of B^S deviations is about the same over the entire plot, i.e., the effect of structural perturbations of comparable stereochemistry vis-à-vis the carbonyl group is of comparable magnitude regardless of ketone class. In addition, a certain amount of bunching may be noted. For example, the preponderance of bicyclooctanones have $\bar{B} > 30 \times 10^{-8}$, while the preponderance of cyclohexanones and decalones lie in the range $(-10 \times 10^{-8}) < \bar{B} < (20 \times 10^{-8})$. These data are a reflection of the fact that significant vibructional effects can accompany alterations in basic skeletal structure even when the C_α-C-$C_{\alpha'}$ angle θ is not greatly changed. In the ketones we have considered, such behavior is most frequently related to changes in the kind and number of forward and rearward α substituents that accompany skeletal change. The importance of such modifications in α substituents has already been noted, e.g., among the cyclopentanones.

Summary

Group theoretical arguments (preceding paper) have shown that the totally symmetric part of a static structural perturbation can exert a synergistic (or antienergistic) effect on the MCD intensity borrowed by vibronic coupling in a forbidden transition. In the present work, the effect is examined numerically for the lowest forbidden singlet transition in saturated ketones.

The term "vibruction" is introuced (Theory A) as a convenient contraction for the phrase "vibrational-structural perturbation". In Theory B, it is recalled that the geometric perturbation (GP) method provides a convenient formalism for the numerical estimation of the vibructional terms, $\bar{B} = (B^V + B^{VS})$. The GP method is then applied to acetone (Theory C) and variations in $\bar{B}$ with variations in ϵ, the dihedral angle for α substituents, and in θ, the C_α-C-$C_{\alpha'}$ bond angle, were noted. The results were then used to generate a stereochemical model for studying vibructional effects in a wide variety of alkyl substituted saturated ketones. Specific expressions from the model are given in Theory C.3, and the pertinent semiempirical nongeometrical constants in Table VII.

The model is found to work reasonably well when applied (Applications) to 72 saturated ketones drawn from classes with disparate skeletal structures. In particular, the model explains changes in $B(n\pi^*)$ values with changes in molecular structure that are puzzling if only static structural perturbations (B^S terms) are invoked. In this connection, the model provides a logical and useful extension to our earlier protocol (ref 9) which concerns itself primarily with the effects wrought by changes in B^S terms.

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References and Notes

(1) (a) Stanford University; (b) University of Minnesota.
(2) (a) Paper 49 in our series Magnetic Circular Dichroism Studies. For part 48, see the preceding paper in this issue. (b) Taken in part from the Ph.D. Dissertations of Kent Morrill and J. Scott Dixon, Stanford University.
(3) (a) C. Djerassi, "Optical Rotatory Dispersion", McGraw-Hill, New York, N.Y., 1960; (b) P. Crabbé, "ORD and CD in Chemistry and Biochemistry", Academic Press, New York, N.Y., 1972.
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(16) We note that a_2 vibrations are thereby omitted from further consideration since these modes produce only z-polarized electric dipole transition moments.
(17) The distorted geometry was calculated as follows: From the eqillibrium geometry the oxygen atom was moved out of plane while holding the CO bond length constant and several CNDO/2 energies were calculated. The final geometry was calculated by interpolating the potential energy to ~394 cm^{-1}, the vibrational frequency reported for this mode.[18] This motion is the analogue of the ν_4 mode in formaldehyde, hence the nomenclature B_4. The basis set for the GP calculations (CI was included) consisted of all excitations from the two highest occupied n orbitals to the lowest π^* and three lowest σ^* virtual orbitals and an excitation from the highest occupied σ orbital to the π^* orbital. This basis set is analogous to the minimal basis set which has been found to be adequate in formaldehyde.[10]
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(33) The nongeometrical constants for eq 18 are obtained from multiple re-

gression analysis of the experimental data. The assumption here is that eq 18 together with the experimental data provide a legitimate basis for a statistical determination of the nongeometrical constants.

(34) An initial regression analysis of all the ketones in Table VI with $\theta \sim 120°$ revealed that 2,2,6,6-tetramethylcyclohexanone (**32**) and *cis*-3,5-di-*tert*-butylcyclohexanone (**39**) differed by more than 2.9 standard deviations from the experimental values. There is also reason to suspect[35,36] that the assumed chair geometries used in calculating the geometrical parameters for these compounds may deviate in an important way from the actual geometries. Hence these compounds and the closely related 2,2,6,6-tetraethylcyclohexanone (**33**) and 3-*tert*-butylcyclohexanone (**35**) were omitted from the analysis. Also omitted were the cyclohexanones with bulky γ substituents, **36, 40,** and **41,** where conformational stabilization is known to affect B values significantly.[9] A further justification for the omissions just noted is given in ref 37, which is best read at the end of this section.

(35) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **52,** 308 (1974).

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(37) In the Theory C.3 section it is noted that different sets of nongeometric constants in eq 18 are necessary for the idealized cyclohexanones, cyclopentanones, and cyclobutanones because of the strong θ dependence of B. Stothers and Tan find evidence[35] from ^{13}C NMR measurements that 2,2,6,6-tetramethylcyclohexanone (**32**) has a flattened chair geometry, and hence there is a concomitant change in θ here from its value in the idealized chair cyclohexanones. Such strained, flattened chairs can best be treated as a separate class of ketones, with their own set of nongeometrical constants. Unfortunately, the paucity of data for such systems at this time precludes determination of the constants. If one can extrapolate from the very limited data at hand, it can be seen by comparing $B(n\pi^*,\mathbf{65}) = 82 \times 10^{-8}$ with $B(n\pi^*,\mathbf{61}) = -20 \times 10^{-8}$ that the contribution from forward out-of-plane α-substituent carbons becomes increasingly negative with increasing θ. If one can extrapolate further to 2,2,6,6-tetramethylcyclohexanone (**32**), then a flattened chair geometry with four forward out-of-plane methyl groups would be consonant with the strongly negative observed $B(n\pi^*,\mathbf{32}) = -176 \times 10^{-8}$. There is also evidence[31] for chair flattening in the case of *cis*-3,5-di-*tert*-butylcyclohexanone (**39**). However, here the affected α substituents are hydrogens, and an analogous extrapolation would lead one to expect a strong positive increment in the B value, in accord with $B(n\pi^*,\mathbf{39}) = 193 \times 10^{-8}$. For the γ-substituted cyclohexanones **35, 40,** and **41,** independent evidence for conformational stabilization can be found in their Raman spectra. Table VIII gives the relative intensities of the Raman band of this series which Fuhrer et al.[21] find to be most clearly associated with the out-of-plane bend ($\nu \sim 655$ cm^{-1}, PE 32%).[21] The dramatic drop in the intensity of the 655-cm^{-1} band with increasing bulk of the γ substituent shows clearly that the nature of the out-of-plane bending motion is significantly and monotonically modified by bulky γ substituents. Such modifications had been inferred previously[9] from the MCD data and their important role in MCD analysis noted.[9]

(38) NOTE ADDED IN PROOF. Recent ab initio energy calculations (M. Askari, N. S. Ostland, and L. Schäfer, *J. Am. Chem. Soc.*, submitted for publication) indicate that the relative populations of the chair–chair conformers of **5** and **6** are >99 and ~75%, respectively. Thus the anomalous MCD behavior noted for **6** may well reflect the presence of a significant population of nonchair forms in that compound.

Low Valent Cobalt Triisopropyl Phosphite Complexes. Characterization of a Catalyst for the Hydrogenation of α,β-Unsaturated Ketones

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Abstract: A group of new low valent cobalt complexes with triisopropyl phosphite ligands (L) has been prepared. Chemically and catalytically, the group was largely distinguished from analogous groups derived from less bulky phosphite ligands. In the cobalt(0) and -(I) classes, all species were tetrahedral and paramagnetic as in CoL_4, CoL_4^+, and CoL_3X; the cobalt(I) class tended to be diamagnetic and five-coordinate at low temperature in coordinating solvents. Alkali metal salts of the Co(−I) species were distinctive in composition, $M^+CoL_5^-$, and in their very high hydrocarbon solubilities. Reaction of η^3-$C_3H_5Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$ with hydrogen produced $H_3Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$, an active catalyst for olefin hydrogenation. A notable catalytic property of this trihydride was its selective hydrogenation of α,β-unsaturated ketones and amides to the saturated ketones and amides.

Cobalt has been a much studied metal center in modern coordination chemistry beginning with the classic investigations by Werner. The focus of these studies has somewhat shifted from cobalt complexes with hard ligands to soft ligands because the latter convey to cobalt a diverse chemistry that has substantial utility in such areas as catalysis. A family of these complexes of special note is derived from phosphine and phosphite complexes.[1-11] Here the more extensive classes are based on cobalt(I) with phosphite and phosphine ligands such as the diamagnetic CoL_5^+ and $HCoL_4$ complexes.[1-11] Within this family, we have sought distinctive chemical and catalytic properties by the employment of large, bulky phosphites and report herein a successful application with the triisopropyl phosphite ligand.

Results and Discussion

Cobalt(−I). Synthetically valuable alkali metal salts of cobalt(−I) complexes, $M^+Co[P(OR)_3]_4^-$ have been prepared with trimethyl and triethyl phosphite ligands[8b] by the reaction of the respective hydrides, $HCo[P(OR)_3]_4$, with alkali metal hydrides. This synthetic procedure failed completely[8b] when applied to $HCo[P(O\text{-}i\text{-}C_3H_7)_3]_4$. This observation was ascribed to a steric shielding of the Co–H bond by the isopropyl phosphite ligands, a hypothesis supported by inspection of carefully constructed moleular models of the five-coordinate hydride. Synthesis of cobalt(−I) triisopropyl phosphite complexes was achieved by the alkali metal amalgam reduction of cobalt(II) chloride in the presence of excess phosphite. These derivatives had two distinctive properties, a composition of the form $MCo[P(O\text{-}i\text{-}C_3H_7)_3]_5$ and a very high solubility in aliphatic hydrocarbons like pentane. Pentacoordinate d^{10} anionic complexes, although not impossible, are extremely unlikely in the light of established d^{10} structural chemistry. The impressive solubility of these $MCoL_5$ complexes in saturated hydrocarbons was in striking contrast to the intractability[9b] of the $M^+Co[P(OR)_3]_4^-$ ($R = CH_3$ and C_2H_5) complexes which did not dissolve in nonprotonic solvents and dissolved with reaction (formation of $HCoL_4$) in protonic solvents. Solubility features and conventional d^{10} structural characteristics may be subsumed in a $MCoL_5$ structure with a tetrahedral d^{10} CoL_4^- unit which partially satisfies the alkali metal cation coordination sphere with phosphite oxygen atoms and a noncobalt bound phosphite ligand which completes the alkali metal coordination sphere.[12] *One* possible representation is depicted in **1.** Solution