Structure and the Magnetic Circular Dichroism of Saturated Ketones[1-3]

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Abstract: A theorem derived from group theoretical principles permits the development of a simple protocol for relating the structures of saturated ketones and the magnetic circular dichroism associated with their lowest singlet n → π* transitions. The method is tested against a series of 22 conformationally well-defined ketones and found to be in accord with experiment.

I. Introduction

That magnetic circular dichroism (MCD) is sensitive to the molecular geometry of carbonyl compounds is suggested by the variety of band shapes and the range of ellipticities exhibited by the MCD data of more than 50 aldehydes and ketones.[4] Moreover, in contrast to the natural circular dichroism (CD) exhibited by chiral ketones,[5] MCD is manifested by achiral systems as well. As such, it has potential utility as a chiroptical method for all carbonyl-containing compounds. Of course, the information to be obtained from MCD measurements will differ from that obtained from CD data. Indeed, the separate physical origins of the two phenomena virtually guarantee such a difference. The differential response of an optically active molecule to left and right circularly polarized light is a consequence of its intrinsically dissymmetric molecular structure, whereas in magnetooptical activity, it is the external magnetic field that provides the proper environment for such a response.

Group theoretical considerations are sufficient to elucidate some of the kinds of information that may be extracted from the MCD spectra of saturated ketones. It is demonstrated in a separate paper[6] that the MCD associated with the symmetry-forbidden carbonyl n → π* transition is of second or higher order in both vibrational and structural perturbations; moreover, that the contributions to the magnetic rotational strengths of perturbations belonging to different irreducible representations are additive. This theorem provides the basis for the development of symmetry rules which relate the molecular geometry of ketones to their magnetic rotational strengths.

The protocol for extracting structural information is developed in detail for the general case. However, in this initial work, we limit ourselves to ketones whose ring conformations are relatively well defined in order to minimize the problems associated with the inevitable incursion of vibrational perturbations at the same level as structural perturbations. Although the set of rules set forth can be applied with ease, the elaboration of their basis is somewhat more complicated. Accordingly, the reader who is more interested in applying the rules rather than in their derivation can skip sections II.B.1 through II.B.3b.

II. Theory

A. Background. The magnetic circular dichroism associated with the transition $a \rightarrow j$ is given by[7,8]

$$[\theta]_{\mathrm{M}} = -\frac{24NH}{\hbar c}\left\{A(a \rightarrow j) f_1(\nu,\nu_{ja}) + \left[B(a \rightarrow j) + \frac{C(a \rightarrow j)}{kT}\right] f_2(\nu,\nu_{ja})\right\} \quad (1)$$

where N is Avogadro's number, H is the magnetic field strength, and ν_{ja} is the resonance frequency of the transition. The line shapes are described by the functions $f_1(\nu,\nu_{ja})$ and $f_2(\nu,\nu_{ja})$.[8] $A(a \rightarrow j)$ is nonzero only if either of the states a or j is degenerate, and $C(a \rightarrow j)$ is nonzero only if state a is degenerate. $B(a \rightarrow j)$ is, in general, nonzero regardless of the existence of ground or excited state degeneracies. Since the carbonyl chromophore does not possess the minimum symmetry required for the existence of essential degeneracies, we will be concerned with the B term exclusively.

In the absence of degenerate states the magnetic rotational strength[9] may be written as[7]

$$-B(a \rightarrow j) = I_m\left\{\sum_{k\neq a}\frac{\langle k|\mu|a\rangle\cdot\langle a|m|j\rangle \times \langle j|m|k\rangle}{E_{ka}} + \sum_{k\neq j}\frac{\langle j|\mu|k\rangle\cdot\langle a|m|j\rangle \times \langle k|m|a\rangle}{E_{kj}}\right\} \quad (2)$$

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[2] Paper XVIII in the Stanford University series Magnetic Circular Dichroism Studies. For part XVII, see: G. Barth, W. Voelter, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 1293 (1972).

[3] Taken in part from the Ph.D. Thesis of Lloyd Seamans, University of Minnesota, 1971.

[4] (a) G. Barth, E. Bunnenberg, and C. Djerassi, *Chem. Commun.*, 1276 (1969); (b) G. Barth, E. Bunnenberg, C. Djerassi, D. Elder, and R. Records, *Symp. Faraday Soc.*, 3, 49 (1969).

[5] (a) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, N. Y., 1960; (b) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965; (c) P. Crabbé, "An Introduction to the Chiroptical Methods in Chemistry," Impressa Offsali, Mexico City, 1971.

[6] L. Seamans and A. Moscowitz, *J. Chem. Phys.*, **56**, 1099 (1972).

[7] P. J. Stephens, W. Suëtaka, and P. N. Schatz, *ibid.*, **44**, 4592 (1966).

[8] (a) A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, 17, 399 (1966); (b) P. J. Stephens, *J. Chem. Phys.*, **52**, 3489 (1970).

[9] There seems to be no unanimity in the literature as to exactly what one means by the phrase "magnetic rotational strength." In fact, the

where m and μ are the electric and magnetic dipole moment operators, respectively, and $E_{mn} = E_m - E_n$. When numerical values of $B(a \rightarrow j)$ are required, we shall use units of (Debye)^2 Bohr magnetons/wave number $\equiv \mathrm{D}^2\,\beta_\mathrm{M}/\mathrm{cm}^{-1}$.

It is apparent from eq 2 that quantitative calculations of $B(a \rightarrow j)$ are exceptionaly difficult since, in principle, detailed knowledge of the entire manifold of quantum mechanical states of the system is required. Furthermore, calculations using a truncated basis may yield results which are origin dependent.[6,10] However, chemically interesting stereochemical and spectroscopic information of a qualitative nature can be extracted from MCD spectra provided that one utilizes group theoretical considerations in conjunction with critical expermental data. This approach is particularly relevant to symmetry-forbidden transitions.[6] We shall elaborate it by way of a specific example: the 300-nm n–π^* transition of ketones.

B. Decomposition of B(n $\rightarrow$ π^*). The symmetries of the ground and three lowest excited singlet states of the simplest molecule containing a carbonyl chromophore, formaldehyde, are given in Table I. The pertinent character and correlation tables are collected in Table II. Examination of the character table for the C_{2v} point group shows that a transition from a nonvibrating ground state to a planar nonvibrating n–π^* state is electric dipole forbidden. As a result, to zero order, $B(\mathrm{n} \rightarrow \pi^*) = 0$. In absorption, the n $\rightarrow$ π^* transition of formaldehyde does gain intensity through the effect of nontotally symmetric vibrations.[11] In other ketones (*vide infra*) allowed character may be acquired by both structural and vibrational perturbations.

Table I. Formaldehyde Electronic States

State	Symmetry[a]	Energy, eV[b]
N (ground)	A_1	0.0
n $\rightarrow$ π^*	A_2	3.5
n $\rightarrow$ σ^*	B_2	7.1
π $\rightarrow$ π^*	A_1	8.0

[a] C_{2v} point group. [b] n $\rightarrow$ π^* energy from ref 15a, others from ref 11.

Table II. Character Tables

C_{2v}		E	C_2	σ_v	σ'_v
z	A_1	1	1	1	1
R_z	A_2	1	1	−1	−1
R_y, x	B_1	1	−1	1	−1
R_x, y	B_2	1	−1	−1	1
		(C_{2v})	C_s	E	σ_v
x, z, R_y		A_1, B_1	A′	1	1
y, R_x, R_z		A_2, B_2	A″	1	−1
		(C_{2v})	C_s'	E	σ_v'
y, z, R_x		A_1, B_2	A′	1	1
x, R_y, R_z		A_2, B_1	A″	1	−1
		(C_{2v})	C_2	E	C_2
z, R_z		A_1, A_2	A	1	1
x, y, R_x, R_y		B_1, B_2	B	1	−1

A perturbation theory treatment of the natural optical activity of saturated ketones leads to rotational strengths which are of first order in the perturbation.[12] The result of this type of treatment is somewhat different in the case of magnetooptical activity in that, as has been demonstrated elsewhere,[6] the magnetic rotational strengths are of second or higher order in the perturbation.[13] This fact makes the theoretical analysis of MCD spectra somewhat more complex than the analysis of CD data. Accordingly, we will consider the problem in some further detail.

Employing the usual perturbation theory formalism, we write the Hamiltonian operator for the carbonyl chromophore as the sum of a zero-order Hamiltonian $\mathbf{H}_0$ and the perturbation operator V. It is necessary here to consider only the symmetry properties of V. This operator may be decomposed into a sum of functions which form bases for the irreducible representations[14] of the point group of the unperturbed system, in this case C_{2v}

$$V = V(\mathbf{A}_1) + V(\mathbf{A}_2) + V(\mathbf{B}_1) + V(\mathbf{B}_2) \qquad (3)$$

The consequence of the theorem proved by Seamans and Moscowitz[6] is that perturbations belonging to different irreducible representations contribute separately to the magnetic rotational strengths associated with a symmetry-forbidden transition. Since it is evident that a totally symmetric perturbation cannot contribute any allowedness to the transition, we may write for a saturated ketone that

$$B(\mathrm{n} \rightarrow \pi^*) = B(\mathbf{A}_2) + B(\mathbf{B}_1) + B(\mathbf{B}_2) \qquad (4)$$

Further, in ketones of C_{2v} symmetry, only vibrational perturbations contribute to the magnetic rotational strength and eq 4 can be written in the more explicit form

$$B(\mathrm{n} \rightarrow \pi^*, C_{2v}) = B(\mathrm{a}_2) + B(\mathrm{b}_1) + B(\mathrm{b}_2) \qquad (5)$$

where the lower case letters, *e.g.*, a_2, refer specifically to vibrational perturbations of that symmetry.[14]

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problem is often met by avoiding use of the phrase itself. In the case of natural optical activity, the rotational strength $R(a \rightarrow j)$ of the transition $a \rightarrow j$ is given by (*mutatis mutandis*, eq 51 in A. Moscowitz in "Advances in Chemical Physics," Vol. IV, I. Prigogine, Ed., Wiley, New York, N. Y., 1962)

$$R(a \rightarrow j) = \hbar c/24\pi N \int [\theta(a \rightarrow j)]/\nu \mathrm{d}\nu$$

For the case of no degeneracies, where only B terms contribute to the magneto-optical activity, we have[7]

$$-B(a \rightarrow j) = \hbar c/12\pi N H \int [\theta(a \rightarrow j)]_\mathrm{M}/\nu \mathrm{d}\nu$$

(The discrepancy of a factor of 2 in the right hand sides of the above equations arises from the basic theoretical definitions of $R(a \rightarrow j)$ and $B(a \rightarrow j)$. It seems reasonable to us then, in the absence of degeneracies, to refer to $(-B(a \rightarrow j))$ as the "magnetic rotational strength" of the transition, and to $B(a \rightarrow j)$ itself as the "B value" for the transition. These definitions have the virtue of associating a positive magnetic rotational strength with a positive MCD curve. (*N.b.*, this is contrary to our usage in ref 6, where $B(a \rightarrow j)$ itself was referred to as the magnetic rationalized strength.)

(10) D. J. Caldwell and H. Eyring, "Theory of Optical Activity," Wiley-Interscience, New York, N. Y., 1971, p 184.

(11) J. A. Pople and J. W. Sidman, *J. Chem. Phys.*, **27**, 1270 (1957).

(12) (a) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); (b) T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, **48**, 3115 (1968).

(13) Terms of the form $\mu\mu\mu$ may be allowed in zero order. However, a simple order of magnitude calculation shows that these terms do not contribute significantly to the magnetic rotational strength of the carbonyl n $\rightarrow$ π^* transition (see ref 3).

(14) Throughout this paper we utilize capital letters in bold face type to denote group representations, capital letters in standard type to denote structural perturbations, and lower case letters to denote vibrational perturbations.

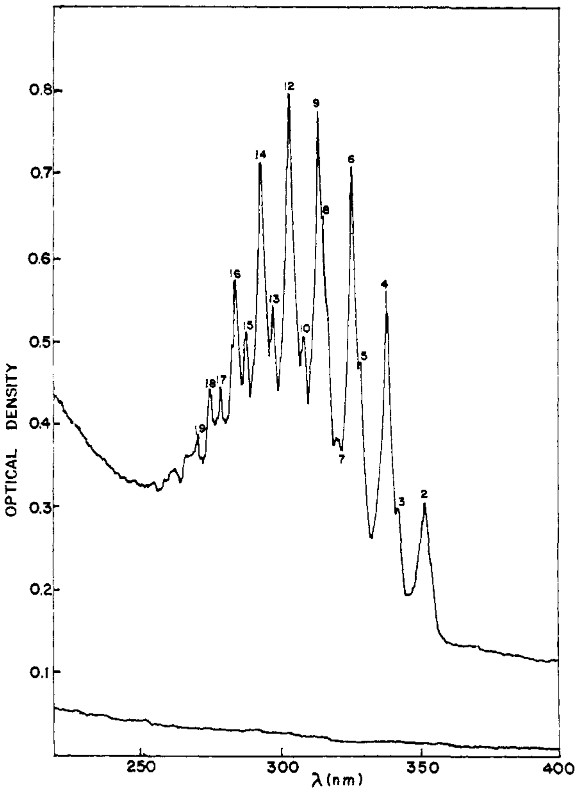

Figure 1a. Absorption spectrum recorded for formaldehyde (**1**) in perfluorohexane at 20°. Although the concentration of formaldehyde is not known measurement was carried out in parallel with the MCD spectrum (see caption, Figure 1b) during the same time period and on aliquots from the same stock solution.

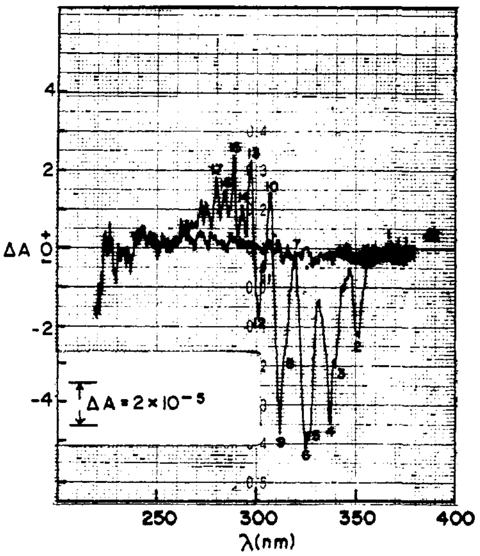

Figure 1b. MCD spectrum recorded for formaldehyde (**1**) in perfluorohexane at 20° (see caption, Figure 1a). Circular dichroism ($A_L - A_R$) is given for a 49.5-k*G* field.

In order to determine *empirically* the signs and relative magnitudes of the vibrational contributions to the magnetic rotational strength, we now need MCD data for a saturated carbonyl-containing molecule whose vibronic states have been characterized in sufficient detail to provide the information required. Such a molecule is formaldehyde.

1. C_{2v} **Ketones**: **Formaldehyde (1).** It is well established that formaldehyde is nonplanar in the excited state and that the barrier to inversion is low, resulting in the inversion doubling which is observable in the uv spectrum[15] and also in the MCD spectrum (Figure 1a and b). Nevertheless, it is convenient to retain the symmetry representations of the C_{2v} point group for the vibronic levels. The normal vibrational modes of formaldehyde are illustrated in Figure 2.[16] The vibrational components of the inversion doublets associated with each quantum of the molecule bending vibration ν_4' have symmetries a_1 and b_1. The corresponding out-of-plane bending vibration in the ground state ν_4'' is of symmetry b_1. The other vibational modes in which we shall be interested are the asymmetric C–H vibration ν_5 and the symmetric C–O stretching vibration ν_2. These vibrational modes are of symmetries b_2 and a_1, respectively.

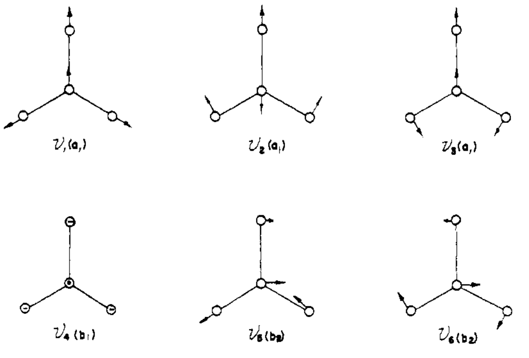

Figure 2. Normal vibrations of the planar formaldehyde molecule (from ref 16).

The notation which we will use for the vibrational progressions is due to Brand[15a] and is shown in the energy level diagram[17] for formaldehyde (Figure 3). In this notation "cold" absorption bands and "hot" bands are denoted by upper case letters and Greek letters, respectively. The subscripts denote the number of quanta of ν_2' which are active in the absorption band and the band origins are labeled with the subscript zero. The band origins A_0, B_0, E_0, and α_0 occur at 28,315, 29,137, 31,187, and 27,036 cm^{-1}, respectively.

The absorption and MCD band assignments are given in Table III. Because of the experimental difficulty caused by the rapid polymerization of formaldehyde in solution as well as the complexity of the spectrum at shorter wavelengths, some of these assignments must be regarded as questionable. The unambiguous assignment of the lower members of the A and B progressions (negative MCD bands) and E progressions (positive MCD bands) is, however, sufficient for our purposes. The very low intensity positive MCD band at the long wavelength side of the spectrum could conceivably be due to the very weak a_0 parallel band (magnetic dipole transition to the lower component of the upper state inversion doublet),[18,19] the n → π* singlet–triplet transition, or to hot bands.

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(15) (a) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956); (b) G. W. Robinson, *Can. J. Phys.*, 34, 699 (1956).

(16) G. W. King, "Spectroscopy and Molecular Structure," Holt, Rinehart and Winston, New York, N. Y., 1964, p 428.

(17) G. Herzberg, "Electronic Spectra and Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 520.

(18) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, 36, 31 (1958).

(19) (a) J. H. Callomon and K. K. Innes, *J. Mol. Spectrosc.*, 10, 166 (1963); (b) J. R. Lombardi, D. E. Freeman, and W. H. Klemperer, *J. Chem. Phys.*, 46, 2746 (1967).

Table III. Uv and MCD Band Assignments for Formaldehyde

Peak no.[a]	Frequency, kK Uv[b]	Frequency, kK MCD[b]	Assignment[c]	Sign of MCD band
1		2.70	α_0 and other hot bands	+
2	2.85	2.84	A_0	−
3	2.93	2.94	B_0	−
4	2.96	2.96	A_1	−
5	3.05	3.06	B_1	−
6	3.08	3.07	A_2	−
7	3.13	3.13	E_0	+
8	3.17	~3.16	B_2	−
9	3.19	3.21	A_3	−
10	3.25	3.25	E_1	+
11		3.29	B_3	−
12	3.30	3.32	A_4	−
13	3.37	3.36	E_2	+
14	3.41	3.41	A_5 (?)	+
15	3.48	3.46	E_3 (?)	+
16	3.53	3.52	A_6 (?)	+
17	3.59	3.57	E_4 (?)	+
18	3.64	(?)	A_7 (?)	+ (?)
19	3.70	(?)	E_5 (?)	+ (?)

[a] Numbering corresponds to that of Figures 1a and 1b. [b] Solvent, perfluorohexane. [c] See discussion in text.

Since the band lies considerably more than 124 cm^{-1} to the red of the A_0 band, it appears doubtful that it is due to the a_0 band. The singlet–triplet transition occurs at 3970 Å[18] while the α_0 band occurs at 3700 Å.[15a] It therefore appears that the MCD bands in question are in fact hot bands and the assignment has been made accordingly. Since the hot bands arise from vibrational perturbations of the ground electronic state rather than the excited state, they are excluded from the subsequent discussion.

The A and B progressions are based on b_1 vibrational modes and the MCD bands associated with these progressions are of negative sign. Therefore, we conclude that for the formaldehyde n → π^* transition, $B(b_1)$ is greater than zero. The E_0 band has been assigned by Brand[15a] to the combination $1_0{}^1 4_0{}^{0-}$ and by Job, Sethuraman, and Innes[20] to $5_0{}^1$. The ν'_1 fundamental is a totally symmetric mode and so, on the basis of the assignments of the A and B progressions, the $1_0{}^1 4_0{}^{0-}$ band would be expected to be associated with an MCD band of negative sign. On the other hand the ν'_5 mode is of symmetry b_2; thus, the observation that positive MCD bands are associated with the E progression is compatible with the assignment of Job, Sethuraman, and Innes.

Since there is no a_2 vibrational mode in formaldehyde, $B(a_2) = 0$. We have thus determined that negative MCD bands will be associated with vibrational progressions based on b_1 modes while progressions based on vibrational modes of symmetry b_2 will show positive MCD bands. In addition, z-polarized transitions, which must of necessity be based on quanta of b_1 symmetry in combination with quanta of b_2 symmetry (or else be magnetic dipole transitions), will be extremely weak, if visible at all, in the MCD spectrum of formaldehyde. We ignore these.

2. Other C_{2v} Ketones. The analysis of the vibrational structure of the MCD spectrum of formaldehyde should also apply to other ketones whose ground states have C_{2v} symmetry. A complication could arise in that, unlike formaldehyde, these molecules will, in general, possess a_2 vibrational modes. However, since these a_2 vibrations involve the extrachromophoric portion of the molecule, one might argue that their effect on the MCD spectrum will be small in many instances. Support for this argument can be found in studies of polarized photoexcitation spectra of ketones[21] which show that these a_2 modes have little influence for the intensity of the absorption spectrum of, for example, cyclohexanone and acetone, even though they have the effect of borrowing intensity from the strongly allowed $\pi \rightarrow \pi^*$ transition. However, we hasten to add that this is not true for all ketones, *e.g.*, cyclobutanone[21b] (*vide infra*).

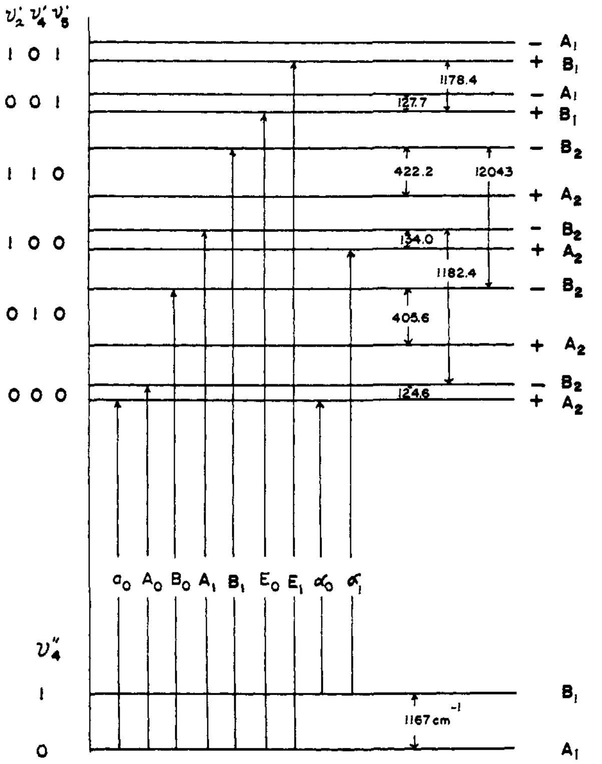

Figure 3. Energy level diagram for formaldehyde (adapted from ref 17).

The MCD spectra of C_{2v} ketones then arise from the superposition of at least three bands, two of which come from progressions based on b_2 vibrational modes and the other from b_1 vibrational perturbations. The former bands will have negative magnetic rotational strengths (B value > 0) while the latter will have positive rotational strengths (B value < 0). The shapes of the MCD curves for different C_{2v} ketones may vary considerably, however, since the relative positions and intensities of the vibrational bands can be expected to vary from molecule to molecule. The MCD spectra of the C_{2v} ketones presented in Figure 4 illustrate such variations that arise because of the intimate relation between structure and vibration.

Adamantanone (**4**) shows only a positive MCD band, which indicates that the contributions of b_1 vibrational modes are suppressed relative to those of the b_2 mode. (Contributions from an a_2 mode have been neglected here.) The probable explanation is that the

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(20) V. A. Job, V. Sethuraman, and K. K. Innes, *J. Mol. Spectrosc.*, **30**, 365 (1969).

(21) (a) W. D. Chandler and L. Goodman, *ibid.*, **36**, 141 (1970); (b) *ibid.*, **35**, 232 (1970).

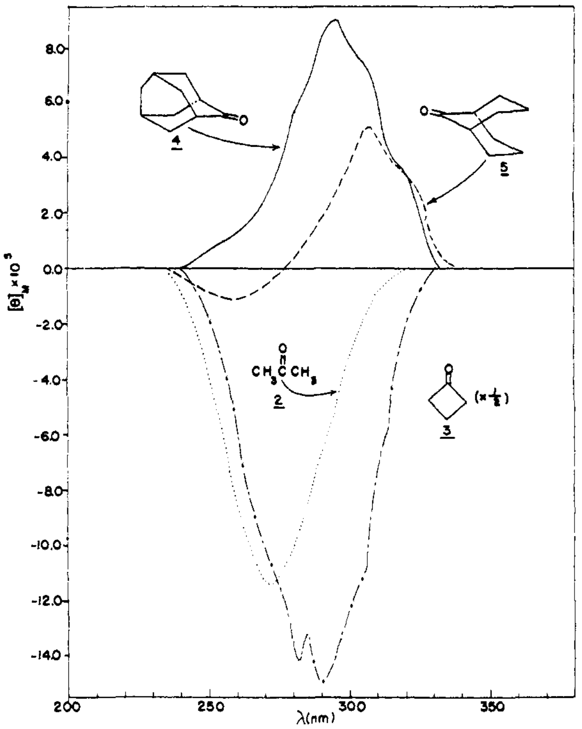

Figure 4. MCD spectra of adamantanone (——), acetone (· · · · ·), cyclobutanone (— — —), and bicyclo[3.3.1]nonan-9-one (- - - -) in cyclohexane. The cyclobutanone curve has been reduced by a factor of 2.

out-of-plane bending motion associated with the b_1 mode is strongly damped by the rigidity of the adamantanone skeleton. Indeed, the out-of-plane motion requires that in the course of vibration the C_α–CO–C'_α angle distort from its equilibrium value (~120°), and this requires concomitant distortion of the relatively rigid molecular framework.

The MCD spectrum of bicyclo[3.3.1]nonan-9-one (**5**) supports our interpretation of the adamantanone spectrum. The spectrum (Figure 4) of **5** exhibits two bands of opposite sign with the positive band much more intense than the negative one. These bands are assigned to progressions based on b_2 and b_1 vibrational modes, respectively. The molecular symmetry of **5** should be approximately C_{2v}: X-ray and infrared studies of the parent hydrocarbon[22] show that the two rings adopt flattened chair–chair conformations wherein the C-3–C-7 hydrogen interaction is relieved by splaying rather than by skewing of the "wings." Its structure, however, is less rigid than that of adamantanone due to the absence of one of the methylene bridges present in the latter molecule. Thus, it might be expected that the b_1 vibrational mode would not be as strongly suppressed as it is in **4**. It is also seen from the MCD spectrum that the maxima in the vibrational progressions have been shifted relative to each other, with the result that the ordering of the positive and negative MCD bands is opposite to that observed in formaldehyde.

Since the barrier to internal rotation of the methyl groups in acetone (**2**) is relatively low (778 cal/mol),[23] this molecule may be considered as roughly a C_{2v} ketone, more similar to formaldehyde than to **4** or **5**. Then, extrapolating from formaldehyde, there is little reason to suspect that the b_1 vibrational modes in acetone will be suppressed. Indeed, the polarized photoexcitation spectra of Chandler and Goodman[21a] indicate that the intensity borrowing in acetone, as compared to formaldehyde, by b_1 vibrations is enhanced relative to the borrowing by b_2 vibrations. The shape of the MCD spectrum of **2** should thus continue the trend established by adamantanone and bicyclo[3.3.1]nonan-9-one. The negative MCD band of **2** shown in Figure 4 is completely in accord with these arguments.

Cyclobutanone (**3**) has been shown to be planar in the ground state but puckered in the excited state.[24] The MCD spectrum of **3** (Figure 4) shows a relatively strong negative band ($[\Theta]_{M,\max} \sim -30 \times 10^{-5}$ compared to -11×10^{-5} for acetone) from which we might conclude that, as in acetone, the b_1 modes are dominant. However, the polarized photoexcitation spectra for **3**[21b] indicate that here the $n \rightarrow \pi^*$ transition obtains intensity predominantly by means of an a_2 vibration that is unusually effective in borrowing electric dipole transition moment. We infer then that the magnetic rotational strength acquired as the result of an a_2 vibration is negative, *i.e.*, $B(a_2) > 0$. The relatively large magnitude found for $B(a_2)$ is also reasonable since an a_2 mode couples the $n \rightarrow \pi^*$ transition with the strongly electric dipole allowed $\pi \rightarrow \pi^*$ transition.

To summarize the results of this section, we have inferred for the C_{2v} ketone that

$$B(b_1) > 0 \tag{6a}$$

$$B(b_2) < 0 \tag{6b}$$

$$B(a_2) > 0 \tag{6c}$$

$$|B(a_2)| > |B(b_1)| \text{ or } |B(b_2)| \tag*{(6d)[25]}$$

3. Ketones of Symmetry Lower than C_{2v}. a. Some Considerations of Structural Perturbations. As has already been mentioned, the $n \rightarrow \pi^*$ transition gains allowed character when the symmetry of the carbonyl chromophore is lower than C_{2v}. Examination of the character tables for the C_{2v} and C_s point groups (Table II) shows that this reduction in symmetry leads to a mixing of the electronic states of the C_{2v} system which is the same as that accomplished by a perturbation of $\mathbf{B}_1$ symmetry. The partial magnetic rotational strength associated with vibrational and structural perturbations of $\mathbf{B}_1$ symmetry then becomes

$$B(\mathbf{B}_1) = B(B_1 + b_1) \tag{7}$$

and for a ketone having C_s symmetry (*e.g.*, the chair form of cyclohexanone)

$$B(n \rightarrow \pi^*, C_s) = B(a_2) + B(B_1 + b_1) + B(b_2) \tag{8}$$

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(22) (a) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); (b) G. Eglinton, J. Martin, and W. Parker, *ibid.*, 1243 (1965).

(23) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, 18, 344 (1965).

(24) (a) J. R. Durig and R. C. Lord, *J. Chem. Phys.*, 45, 61 (1966); (b) A. Bauder, F. Tank, and Hs. H. Günthard, *Helv. Chim. Acta*, 46, 1453 (1963); (c) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 49, 221 (1968); (d) R. F. Whitlock and A. B. F. Duncan, *ibid.*, 55, 218 (1971).

(25) An inequality such as eq 6d cannot be completely general, but will depend on the amplitudes of vibration and the equilibrium coordinates of the nuclei involved in the vibrational modes. Equation 6d is meant to apply to modes involving nuclei of comparable equilibrium coordinates and with comparable amplitudes of displacement.

where, as noted previously, ordinary capital letters denote a structural perturbation. A reduction in the symmetry of the molecule to C_s' corresponds to a perturbation of $\mathbf{B}_2$ symmetry in the C_{2v} point group. The magnetic rotational strength for a ketone belonging to C_s', such as bicyclo[2.2.1]octan-2-one, may then be written as

$$B(\text{n}-\pi^*, C_s') = B(\text{a}_2) + B(\text{b}_1) + B(B_2 + \text{b}_2) \quad (9)$$

The situation in the case of a reduction in symmetry from C_{2v} to C_2 is the same as that brought about by a perturbation of $\mathbf{A}_2$ symmetry, and hence the magnetic rotational strength of, for example, cyclopentanone or the twist conformer of cyclohexanone is given by

$$B(\text{n} \rightarrow \pi^*, C_2) = B(\text{A}_2 + \text{a}_2) + B(\text{b}_1) + B(\text{b}_2) \quad (10)$$

The most common situation is, however, the absence of all elements of symmetry. In this case the perturbation can always be expressed as a sum of perturbations which have the transformation properties of the irreducible representations of the C_{2v} point group. Therefore, the total magnetic rotational strength associated with the n → π* transition of the general saturated ketone may be written as

$$B(\text{n} \rightarrow \pi^*, C_1) = B(\text{A}_2 + \text{a}_2) + B(B_1 + \text{b}_1) + B(\text{B}_2 + \text{b}_2) \quad (11)$$

b. Magnetic Rotational Strengths. Separability of Vibrational and Structural Perturbations. What we seek now is a means of estimating the signs and relative magnitudes of the separate terms on the right side of eq 10. Once such a procedure has been found, in any particular case it becomes a simple matter to add them up and compare the $B(\text{n} \rightarrow \pi^*)$ value with experiment. It is this point to which we address ourselves now.

On the assumption that it is the symmetry of the perturbation that is crucial for the determination of sign, we might carry over eq 6 *in toto* and equate the sign of $B(\text{A}_2 + \text{a}_2)$ with the sign of $B(\text{a}_2)$, etc. Basically, the assumption is a good one. A purely structural perturbation of a given symmetry is akin to a vibrational perturbation of the same symmetry but with an infinitely long period of vibration. Insofar as it is the symmetry of the perturbation that determines which states mix among themselves to give a nonvanishing magnetic rotational strength of a given sign, it is reasonable, *prima facie*, to take $B(\text{A}_2 + \text{a}_2)$ as having the same sign as $B(\text{a}_2)$, etc. However, one of our primary objectives is the acquisition of structural information, and so from this objective we are interested more in the sign and magnitude of $B(\text{A}_2)$ rather than of $B(\text{A}_2 + \text{a}_2)$, and it is herein that our difficulty lies.

As noted earlier, the magnetic rotational strengths are of second or higher order in the perturbation, and the contributions from perturbations belonging to *different* irreducible representations are simply additive. However, the contributions of vibrational and structural perturbations belonging to the *same* irredicible representation are not simply additive, *e.g.*

$$B(\text{A}_2 + \text{a}_2) \neq B(\text{A}_2) + B(\text{a}_2) \quad (12)$$

In other words, the introduction of a substituent into a molecule not only modifies the vibrational possibilities available, but also couples the structural and vibrational consequences for the MCD spectrum in a troublesome way. At this stage we propose to meet the difficulty by considering primarily differences among members of groups of ketones having the same ring size and similar ring conformation. This is tantamount to assuming that within such a group of ketones, eq 12 and its analogs virtually are equalities, so that the difference observed for $B(\text{n} \rightarrow \pi^*)$ values are due primarily to differences in the values of $B(\text{B}_1)$, $B(\text{B}_2)$, and $B(\text{A}_2)$. As we shall see, this will for the most part turn out to be a good assumption although we must be prepared for breakdowns. In fact, we can anticipate when they will occur. It will be easier, however, to elaborate this point after we have shown how to identify the irreducible representation to which a particular structural perturbation belongs.[26]

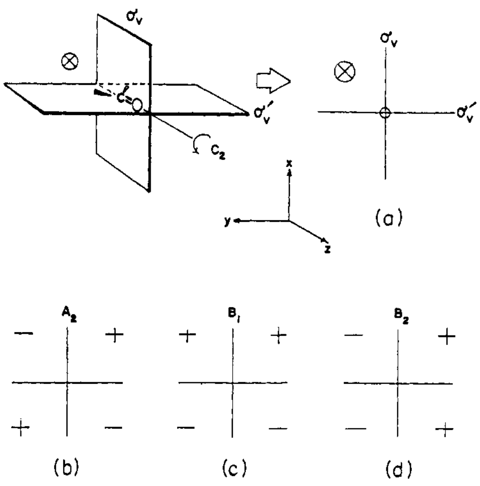

Figure 5. Symmetry operations and projection diagrams for the carbonyl chromophore. ⊗ denotes a perturbing atom.

c. Identification and Classification of a Structural Perturbation. The protocol for the identification and classification of a perturbation associated with the extrachromophoric molecular environment of the carbonyl group is illustrated in Figure 5. The symmetry operations of the C_{2v} point group divide the space surrounding the carbonyl chromophore into four sectors. However, for the purpose of describing the symmetry rules which relate the molecular structure of a saturated ketone to its magnetic rotational strength, it is more convenient to use the planar-quadrant projection shown in Figure 5a.

Examination of the character table for the C_{2v} point group (Table II) shows that functions belonging to the $\mathbf{A}_2$ representation are symmetric with respect to the C_2 group operation but antisymmetric with respect to reflection in the σ_v and σ_v' planes. We represent this behavior by the projection diagram of Figure 5b, using an arbitrary sign convention *that in no way affects the ultimate sign achieved for the magnetic rotational strength.* Functions belonging to the irreducible representation $\mathbf{B}_1$ are antisymmetric with respect to the C_2 and σ_v' operations, and symmetric with respect to σ_v, whereas functions belonging to $\mathbf{B}_2$ are symmetric

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(26) Note: It has been pointed out to us by a referee that the Ph.D. thesis of G. M. Robinson, Tulane University, 1970, contains some of the results noted here. Namely, the thesis shows that, for the n-π* transition in saturated ketones, the magnetic rotational strength must be of second or higher order in the perturbation and that vibronic coupling and structural perturbations can contribute comparably to the magnetic rotational strength.

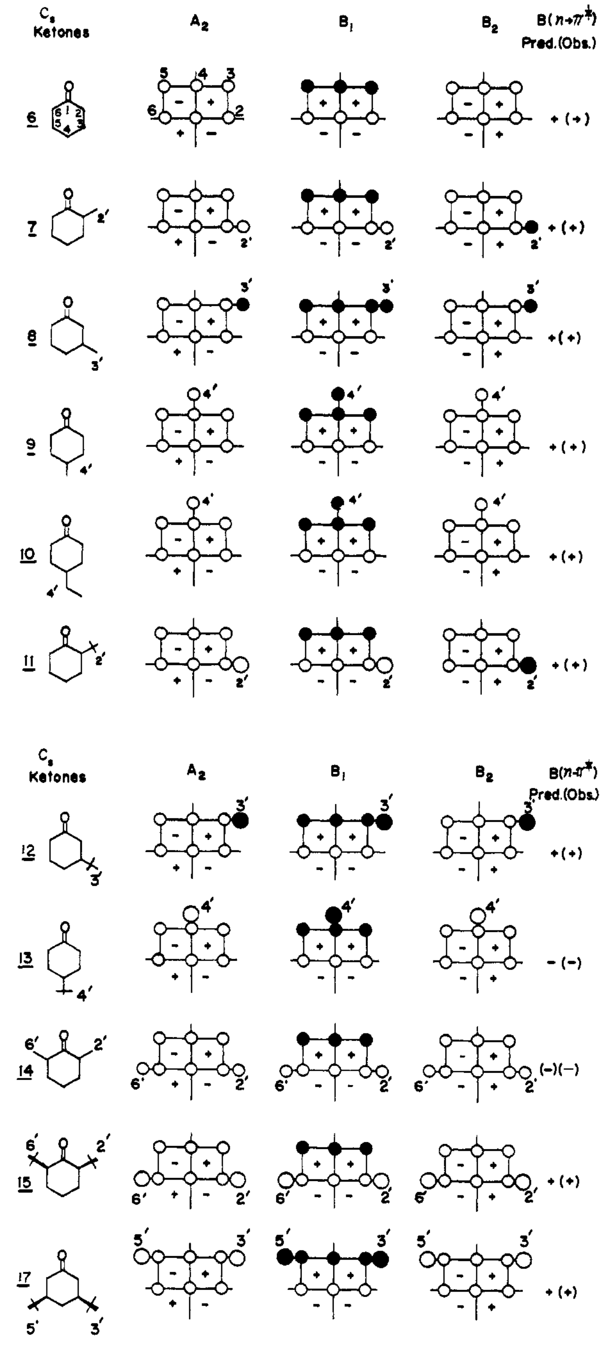

Figure 6. Projection diagrams for chair cyclohexanones. The perturbing atoms are indicated here and elsewhere by the darkened circles. Larger circles are used for the *tert*-butyl group. The ambiguity of the prediction for **14** is discussed in the text.

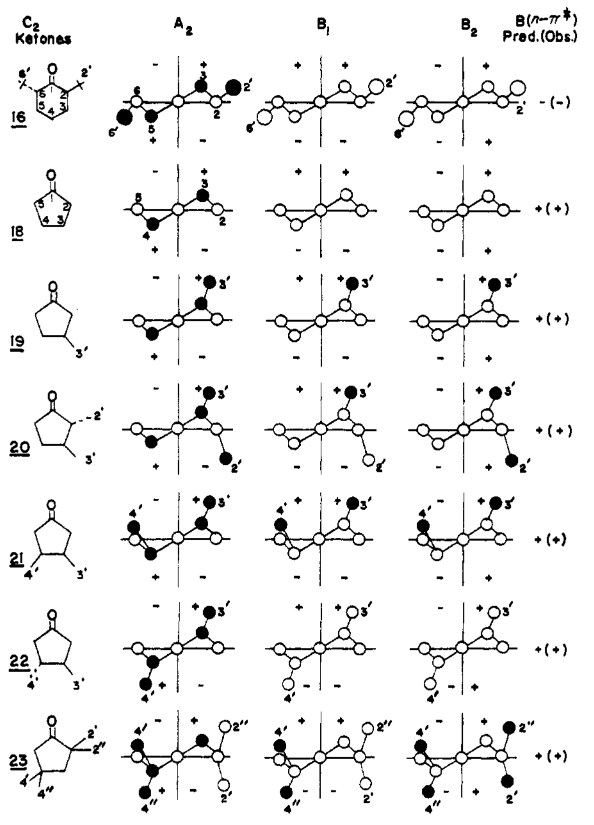

Figure 7. Projection diagrams for ketones having twist ring conformations.

under σ_v' and antisymmetric with respect to C_2 and σ_v. The projection diagrams for B_1 and B_2 are given in Figures 5c and 5d, respectively.

All that is necessary now is to project a molecule onto the diagrams and classify the perturbing atoms. For example, consider the carbon atoms of chair cyclohexanone, whose projections are shown in Figure 6. In the A_2 diagram, atoms 3 and 5 are symmetrically disposed in positive and negative quadrants and thereby cancel the effect of each other. Atoms 2 and 6 as well as 1 and 4 lie on the horizontal and vertical nodal planes and consequently do not contribute to $B(\mathrm{n} \rightarrow \pi^*)$. Hence, $B(A_2) = 0$. Similarly, there is a complete cancellation in the B_2 diagram owing to the vertical nodal plane, and $B(B_2) = 0$. In the case of B_1, however, although atoms 1, 2, and 6 give no contribution since they lie on a nodal plane, there is a net contribution from atoms 3, 4, and 5. Hence $B(B_1) \neq 0$. The hydrogen atoms of cyclohexanone also would contribute only to $B(B_1)$. Therefore, for the chair conformer of cyclohexanone, the only structural contributions to $B(\mathrm{n} \rightarrow \pi^*)$ we need consider are those associated with $B(B_1)$.

Decomposition of $B(\mathrm{n} \rightarrow \pi^*)$ for any ketone can be made in this simple way. The pertinent diagrams for the molecules considered in this work are collected in Figures 6, 7, and 8. The perturbers which contribute to $B(\mathrm{n} \rightarrow \pi^*)$ are indicated by darkened circles, whereas atoms which do not contribute are indicated by open circles. The projections shown have been made with some further simplifying assumptions.

In this initial work, for the sake of simplicity, we limit ourselves to alkyl perturbers and treat methylene ring groups and the methyl, ethyl, and *tert*-butyl substituents as single pseudoatoms. Hence, the hydrogen atoms do not appear explicity in the diagrams. In addition, α-equatorial substituents (pseudoatoms) are assumed to lie in the carbonyl plane. With regard to these simplifications, the pertinent caveats of the octant rule,[27] such as those contained in footnotes 11 and 17 of ref 27, obtain here also.

With this introduction to the identification of the irreducible representations to which a particular structural perturbation belongs, we return now to the questions of the signs to be associated with the component $B(A_2)$, $B(B_1)$, and $B(B_2)$ values,

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[27] W. Moffit, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 83, 4013 (1961).

d. Signs and Magnitudes of Structural Contributions to $B(\mathrm{n} \rightarrow \pi^*)$. In view of the discussion of section 3b, it is tempting to attribute to $B(\mathrm{A}_2)$, etc., the signs arrived at empirically for $B(\mathrm{a}_2)$, etc. However, it must be remembered that the empirical assignments were obtained using model compounds in which the vibrations involved atomic displacements lying to the rear of the carbonyl chromophore. Hence these signs would be most appropriate for structural perturbations that also lie to the rear of the carbonyl group. The question arises, "What about perturbers which are to the front of the carbonyl group, or nearly so?" It is difficult to answer this question with any confidence at the present time. However, a simple molecular orbital calculation based on a coulombic potential indicates that the partial magnetic rotational strength associated with an A_2 structural perturbation would change sign somewhere in the vicinity of the carbon atom of the carbonyl group. The calculation is crude, and the region over which $B(\mathrm{A}_2)$ is predicted to change sign is highly sensitive to the molecular orbital coefficients chosen. In the set of compounds considered in this paper, the question of sign change for $B(\mathrm{A}_2)$ arises only in the case of **16**. As a tentative working protocol, we take $B(\mathrm{A}_2)$ to change sign along the z-direction at the position of the carbonyl carbon atom. However, we should be prepared for a modification of this rule at some later date.

There are even more difficulties associated with a similar investigation of $B(\mathrm{B}_1)$ and $B(\mathrm{B}_2)$ because of the problem of origin dependence.[6,10] We will just note here that calculations performed in the same spirit as those described for $B(\mathrm{A}_2)$ indicate no sign change for $B(\mathrm{B}_1)$ and $B(\mathrm{B}_2)$.

In the light of the discussion of this section, section 3b and eq 6, we may now summarize the signs and relative magnitudes for the component B values as follows

$$B(\mathrm{B}_1) > 0 \qquad (13\mathrm{a})$$

$$B(\mathrm{B}_2) < 0 \qquad (13\mathrm{b})$$

$$B(\mathrm{A}_2)\begin{cases} > 0, \text{ perturber to rear of carbonyl carbon} \\ < 0, \text{ perturber forward of carbonyl carbon} \end{cases} \qquad (13\mathrm{c})$$

$$|B(\mathrm{A}_2)| > |\mathrm{B}(B_1)| \text{ or } |B(B_2)| \qquad (13\mathrm{d})^{28}$$

e. The Conformational Stabilization Rule. The only point remaining to complete the protocol concerns the breakdown of the assumption concerning the use of $B(\mathrm{A}_2)$, etc., in place of $B(\mathrm{A}_2 + \mathrm{a}_2)$, etc., raised at the end of section 3b.

All other things being equal, the effectiveness of a particular vibration for generating magnetic rotational strength depends on its amplitude: the larger the amplitude, the larger the magnitude of the associated B value. Hence, any modification that diminishes the amplitude of a vibration will also suppress the contribution of that vibration to the magnetic rotational strength. Since an increase in force constant means a decrease in amplitude, any structural perturbation that stiffens a force constant will diminish the effectiveness of that mode for generating magnetic rotational strength, and the greater the stiffening, the less effective the vibration.

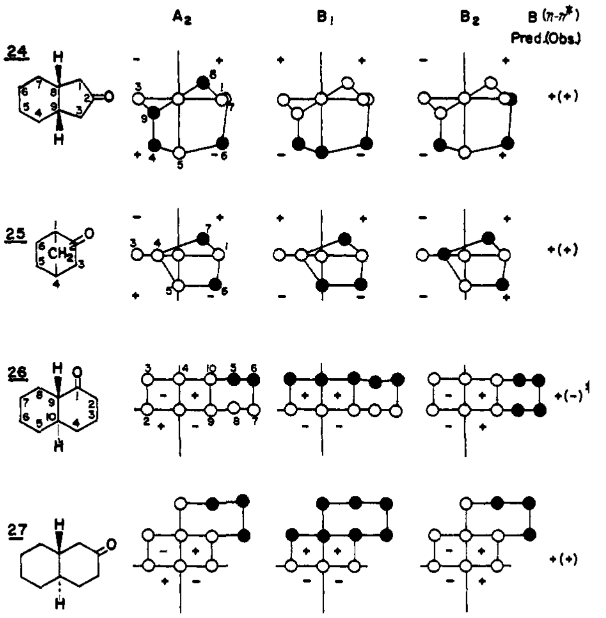

Figure 8. Projection diagrams for fused and bridged ring ketones.

The introduction of a substituent frequently causes such a stiffening. For example, it is well known that the introduction of a 4-*tert*-butyl group stabilizes the chair form of cyclohexanone which belongs to the C_s point group.[29a] Therefore, insertion of a 4-*tert*-butyl group into a chair cyclohexanone increases the force constant for the totally symmetric vibration in the C_s point group. The totally symmetric representation $\mathbf{A}'$ in C_s correlates with the $\mathbf{B}_1$ representation in C_{2v} (see Table II). Hence, with the introduction of a 4-*tert*-butyl group (which, as we shall see from the appropriate projection diagrams in Figure 6, contributes as a pure B_1 structural perturbation) we must be prepared also to subtract off something that contributes as $B(\mathrm{B}_1)$. Similar considerations and examination of the correlations in Table II for C_s' and C_2 require similar subtractions that contribute as $B(\mathrm{B}_2)$ and $B(\mathrm{A}_2)$, respectively.

We may therefore enumerate the "conformational stabilization rule" as follows. Any structural perturbation that stabilizes a conformation of a particular symmetry requires subtraction of a contribution to a particular component B value. The relevant component B's are, in summary

Conformational symmetry	Examples	Component B value reduced in magnitude
C_s	Chair cyclohexanone	$B(\mathrm{B}_1)$
C_s'	Bicyclo[2.2.2]octan-2-one	$B(\mathrm{B}_2)$
C_2	Twist cyclohexanone	$B(\mathrm{A}_2)$
C_2	Twist cyclopentanone	$B(\mathrm{A}_2)$

III. Applications

Although the MCD spectra of a number of ketones will be presented and briefly commented upon, we emphasize that it is the *total* $B(\mathrm{n} \rightarrow \pi^*)$ value obtained by integration of the total MCD curve for the $\mathrm{n} \rightarrow \pi^*$

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[28] Equation 13d, like eq 6d, cannot be completely general, but will depend on the coordinates of the perturber, in particular, on its disposition relative to the pertinent nodal planes of the projection diagram.

(29) (a) C. Actona and M. Sundaralingam, *Tetrahedron*, **26**, 925 (1970), a discussion of empirical valence-force calculations on possible deviations from exact C_s symmetry due to the equatorial 4-*tert*-butyl group; (b) N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *J. Amer. Chem. Soc.*, **88**, 2999 (1966).

Table IV. MCD and Absorption Spectral Data for Saturated Ketones[a]

Compound[b]	Absorption[c] λ_{max} (ϵ)	MCD[d] λ_{max} ($[\theta]_M \times 10^5$)	$B(n-\pi^*)^{e,f}$ $\times 10^8$	$D(n-\pi^*)^{f,g}$ $\times 10^2$
2 Acetone	278 (13)	275 (−11)	47.0	2.3
3 Cyclobutanone	282 (18)	290 (−30)	146.0	2.9
4 Adamantanone	292 (16)	295 (9)	−36.5	2.5
5[h] Bicyclo[3.3.1]nonan-9-one	294 (16)	306 (5) 260 (−1)	−13.1	2.7
6 Cyclohexanone	289 (15)	311 (2) 275 (−4)	5.5	2.5
7 2-Methylcyclohexanone	288 (18)	314 (3) 275 (−3)	1.8	2.8
8 3-Methylcyclohexanone	288 (17)	280 (−6)	27.2	2.8
9 4-Methylcyclohexanone	289 (20)	315 (1) 275 (−10)	30.3	3.4
10 4-Ethylcyclohexanone	290 (16)	311 (2) 272 (−3)	7.00	2.5
11 2-*tert*-Butylcyclohexanone	295 (20)	273 (−2)	9.5	3.2
12 3-*tert*-Butylcyclohexanone	285 (17)	290 (−11)	53.2	2.8
13 4-*tert*-Butylcyclohexanone	290 (19)	304 (4)	−10.1	2.9
14[i] *cis*-2,6-Dimethylcyclohexanone	286 (18)	307 (2.0) 263(−1)	−1.7	2.6
15[j] *cis*-2,6-Di-*tert*-butylcyclohexanone	302 (17)	321 (−1.7) 275(−1)	6.4	2.7
16[j] *trans*-2,6-Di-*tert*-butylcyclohexanone	308 (50)	314 (4) 263(−2)	−9.2	6.8
17[k,l] *cis*-3,5-Di-*tert*-butylcyclohexanone	280 (28)	265 (−43)	193.0	4.6
18 Cyclopentanone	297 (14)	289 (−19)	95.4	2.4
19 3-Methylcyclopentanone	296 (19)	288 (−23)	109	3.0
20 *trans*-2,3-Dimethylcyclopentanone	297 (22)	288 (−14)	79.1	3.3
21 *cis*-3,4-Dimethylcyclopentanone	297 (21)	286 (−20)	106	3.8
22 *trans*-3,4-Dimethylcyclopentanone	297 (20)	290 (−28)	153	3.1
23 2,2,4,4-Tetramethylcyclopentanone	299 (22)	305 (+9) 270 (−14)	15.2	3.1
24[m] *cis*-2-Hydrindanone	290 (20)	300 (−27)	120	3.0
25 Bicyclo[2.2.1]heptan-2-one	294 (23)	278 (−4)	19.3	3.3
26 *trans*-1-Decalone	290 (22)	300 (5) 258(−3)	−4.1	3.4
27 *trans*-2-Decalone	288 (17)	318 (1.5) 277 (−10)	37.7	2.62

[a] Spectrograde cyclohexane. [b] Data taken from ref 4b except as noted. [c] Wavelength in nm; molar extinction coefficient in M^{1-} cm^{-1}. [d] Molecular magnetic ellipticity in deg dl dm^{-1} mol^{-1} G^{-1}. [e] B value (see ref 9) in units of (Debye)^2 Bohr magneton cm^{-1}. [f] Integration performed over entire n–π* band after accounting for the contribution from small amounts of α,β-enone impurities (<0.5%). [g] Dipole strength in (Debye)^2 cm^{-1}. [h] R. B. Woodward and C. S. Foote, *Tetrahedron*, **20**, 687 (1964). [i] F. S. Johnson, *Chem. Commun.*, 1448 (1969). [j] B. Rickborn, *J. Amer. Chem. Soc.*, **84**, 2414 (1962). [k] N. L. Allinger and F. M. Karkowski, *Tetrahedron Lett.*, 2171 (1965). [l] M. Hanack and K.-W. Heinz, *Justus Liebigs Ann. Chem.*, **682**, 75 (1965). [m] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

transition that provides the principal basis for the comparisons we shall make when analyzing the experimental data.

A. Chair Cyclohexanones. In this series we choose cyclohexanone (**6**) itself as the reference compound. We assume that the chair conformer is the predominant form in solution at normal room temperature, although in a more detailed analysis specific account would have to be taken of contributions from the other conformers present. The projection diagrams are shown in Figure 6 where primed numbers are used for the alkyl substituent. As noted previously, the only structural perturbation belongs to B_1. According to eq 13a, $B(B_1) > 0$. We predict then that B(n–π*, **6**) > 0, in accord with experiment (Table IV). The MCD spectrum of **6** is shown in Figure 9. The positive structured MCD band is attributed to contributions from b_2 *vibrational* perturbations whereas the negative MCD band is attributed to both vibrational and structural perturbations belonging to the irreducible representation B_1, and possibly from a_2 vibrational modes as well.

The projection diagrams in Figure 6 for 4-methylcyclohexanone (**9**) show that, as compared to cyclohexanone, there is an additional B_1 structural perturbation arising from the 4-methyl substituent. We therefore predict B(n → π*, **9**) > B(n–π*, **6**), and this is in conformity with the experimental B(n → π*) values of 30.3 × 10^{-8} and 5.5 × 10^{-8} D^2 β_M/cm^{-1}, respectively.

For 3-methylcyclohexanone (**8**), Allinger[29b] has estimated that the equatorial 3-methyl chair conformer predominates in solution at room temperature to the extent of 90%; consequently, we neglect contributions from other possible conformers. The projection diagrams indicate structural contributions to all three component B values. From eq 13b, a B_2 structural perturbation contributes negatively to B(n → π*) whereas A_2 and B_1 structural perturbations contribute positively. Consequently, from inspection of the diagrams, we expect B(n → π*, **8**) > B(n–π*, **6**), again in accord with experiment (Table IV).

In the case of 2-methylcyclohexanone (**7**), there is a B_2 structural perturbation in addition to the three B_1 structural perturbations of the reference ketone cyclohexanone (**6**). Hence, we predict B(n → π*, **6**) > B (n–π*, **7**) > 0, and this is confirmed by experiment (Table IV).

The case of *cis*-2,6-dimethylcyclohexanone (**14**) is interesting. If one invoked only eq 13, one would pre-

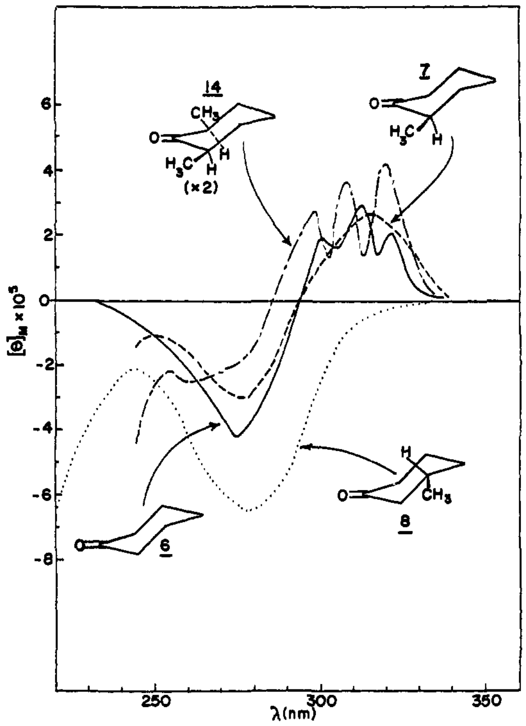

Figure 9. MCD spectra of cyclohexanone (——), 2-methylcyclohexanone (-----), 3-methylcyclohexanone (·····), and *cis*-2,6-dimethylcyclohexanone (— — —) in cyclohexane.

dict that $B(n \rightarrow \pi^*, \mathbf{14}) \approx B(n \rightarrow \pi^*, \mathbf{6})$. However, the presence of the equatorial 2,6-dimethyl substituents stabilizes the chair form relative to cyclohexanone. Hence, invoking the conformational stabilization rule also, we predict $B(n\text{–}\pi^*, \mathbf{14}) < B(n\text{–}\pi^*, \mathbf{6})$, in agreement with experiment. At this stage, it is difficult *a priori* to quantify the stabilization effect and hence to predict whether $B(n \rightarrow \pi^*, \mathbf{14})$ is positive or negative. We have indicated this by the parentheses in the "predicted" column of Figure 6. In the future, one might attempt to get empirical values of heuristic utility from examination of suitable model compounds.

We consider now some *tert*-butylcyclohexanones. In the projection diagrams we have used a larger circle for the *tert*-butyl group as compared to the methyl group to call attention to the approximation of treating it as just a relatively large pseudoatom. The suppression of contributions from different rotomers that follows from the pseudoatom approximation is probably more serious in the case of *tert*-butyl as compared to methyl, although no serious qualitative difficulties arise.

The $B(n \rightarrow \pi^*)$ value of 3-*tert*-butylcyclohexanone (**12**) is almost twice that of $B(n \rightarrow \pi^*)$ for 3-methylcyclohexanone (**8**), and both values are considerably larger than that for $B(n \rightarrow \pi^*, \mathbf{6})$. The value for *cis*-3,5-di-*tert*-butylcyclohexanone (**17**) is still larger, as indeed it should be. All $B(n \rightarrow \pi^*)$ values are of the correct sign.

The projection diagrams for *cis*-2,6-di-*tert*-butylcyclohexanone (**15**) indicate the same $B(n \rightarrow \pi^*)$ values for **15** and cyclohexanone (**6**). In view of the pseudoatom approximation this statement is in good accord with the experimental values $B(n \rightarrow \pi^*, \mathbf{15}) = 6.4 \times 10^{-8}$ and $B(n \rightarrow \pi^*, \mathbf{6}) = 5.5 \times 10^{-8}$. For 2-*tert*-butylcyclohexanone (**11**), one predicts $B(n \rightarrow \pi^*, \mathbf{11}) < B(n \rightarrow \pi^*, \mathbf{6})$. In actual fact, it is somewhat greater: $B(n\text{–}\pi^*, \mathbf{11}) = 9.5 \times 10^{-8}$ and $B(n \rightarrow \pi^*, \mathbf{6}) = 5.5 \times 10^{-8}$. Here, the pseudoatom approximation may be causing the difficulty. In any case, the sign is correctly given.

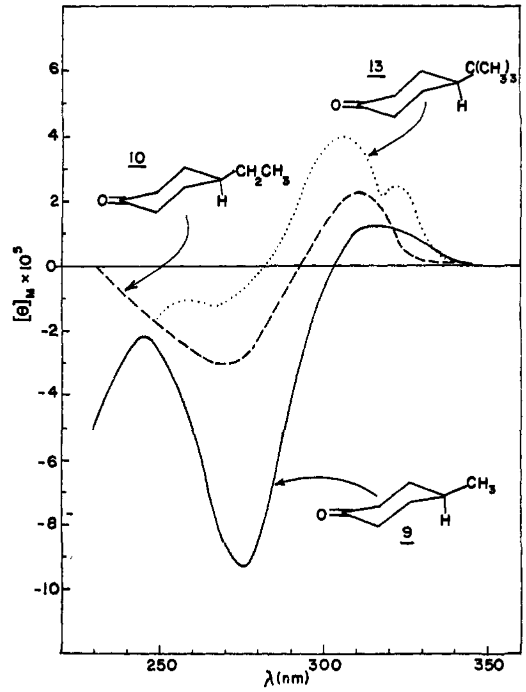

Figure 10. MCD spectra of 4-methyl- (——), 4-ethyl- (-----), and 4-*tert*-butylcyclohexanone (·····) in cyclohexane.

The data for 4-*tert*-butylcyclohexanone (**13**) taken in conjunction with those for 4-ethylcyclohexanone (**10**) and 4-methylcyclohexanone (**9**) provide a good illustration of the conformational stabilization rule. The MCD curves are shown in Figure 10. It will be noted that there is a progression in the relative magnitudes of positive and negative components of the separate MCD curves. As one goes from 4-methyl- to 4-ethyl- to 4-*tert*-butylcyclohexanone, the longer wavelength positive component increases in magnitude, while the negative component decreases in magnitude. This is consonant with the increase in the stabilization of the C_s chair form as the 4-substituent gets heavier, for the greater the stabilization, the greater the contribution that goes as $B(B_1)$ that must be subtracted off. Again, the absolute magnitude of the stabilization effect is difficult to gauge *a priori*, but it is probable that a more quantitative analysis of this series of compounds would be helpful in this regard. For example, from the experimental value $B(n \rightarrow \pi^*, \mathbf{13}) = -10.1 \times 10^{-8}$, one sees that the stabilizing effect of the heavy 4-*tert*-butyl group is sufficient to outweigh the effects of the B_1 structural perturbation. Undoubtedly temperature dependent MCD would be useful in this connection also.

B. Twist Cyclohexanones. Because of the uncertainties in precise geometry and population ratios of conformers attendant on flexible cyclohexanones, we consider here just the case of *trans*-2,6-di-*tert*-butylcyclohexanone (**16**) where the twist form may reasonably be assumed to predominate at ambient temperatures. It is of special interest since the *tert*-butyl substituents project into the region forward of the carbonyl carbon atom. From the projection diagrams (Figure 7)

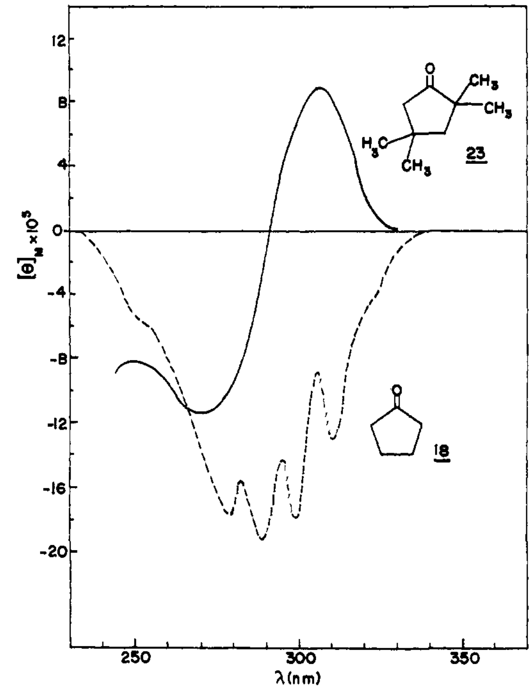

Figure 11. MCD spectra of cyclopentanone (-----) and 2,2,4,4-tetramethylcyclopentanone (——) in cyclohexane.

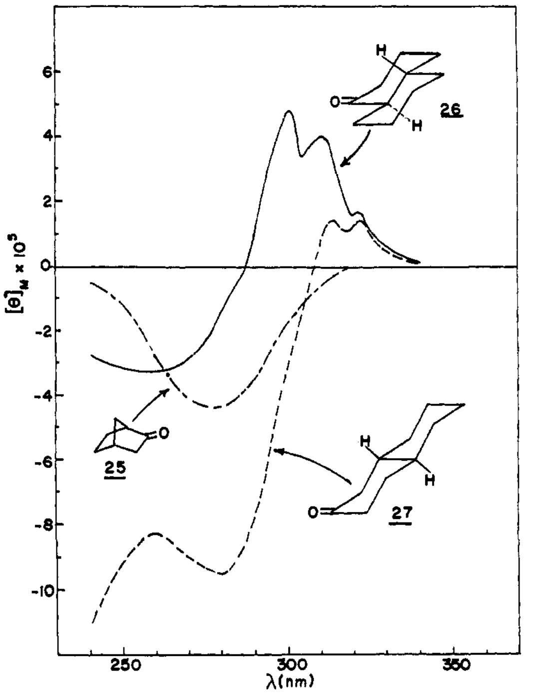

Figure 12. MCD spectra of *trans*-1-decalone (——), *trans*-2-decalone (-----), and bicyclo[2.2.1]heptan-2-one (— — —) in cyclohexane.

we see that the structural perturbation is just A_2, and each *tert*-butyl pseudoatom is paired off *against* an α-methylene pseudoatom (*e.g.*, the 2-*tert*-butyl group *vs.* the C-5 methylene). Since we expect the effect of the larger *tert*-butyl pseudoatom to dominate, we predict a negative sign for $B(n \rightarrow \pi^*, \mathbf{16})$. The experimental value is -9.2×10^{-8}.

C. Cyclopentanones. Microwave studies[30] show that cyclopentanone (**18**) assumes a twist (C_2) conformation in its ground state. Consequently, as the projection diagrams show, there is only an A_2 structural perturbation. As such, we predict $B(n-\pi^*, \mathbf{18}) > 0$ and the measured value is 95.4×10^{-8}. The relatively large value is undoubtedly related in part to the vibration of a_2 symmetry that is important for the borrowing of electric dipole intensity,[21b,30c] from the $\pi \rightarrow \pi^*$ transition.

The projection diagrams for some substituted cyclopentanones are collected in Figure 7, and the pertinent $B(n \rightarrow \pi^*)$ values require little discussion. All the geometrics are dominated by A_2 structural perturbations. In accord with this situation, the experimental $B(n \rightarrow \pi^*)$ values are all positive and there are no particular surprises in their ordering. We shall comment specifically only on 2,2,4,4-tetramethylcyclopentanone (**23**), to date, the only monocyclic cyclopentanone whose $n \rightarrow \pi^*$ MCD curve exhibits oppositely signed components (Figure 11).

Examination of Dreiding models for **23** indicates (a) that the repulsions between the *cis*-methyl groups at positions 2 and 4 will tend to flatten the ring and (b) that these same repulsions will stiffen the force constant for the totally symmetric twisting mode in C_2. As we have seen (*vide supra*), this increase in force constant requires subtraction of an A_2 contribution. Both effects will tend to make $B(n-\pi^*, \mathbf{23}) < B(n-\pi^*, \mathbf{18})$, as is found experimentally. The positive portion of the MCD curve is undoubtedly a reflection of the suppression of these vibrational and structural contributions belonging to A_2.

D. Polycyclic Systems. The projection diagrams for a number of fused and bridged ring ketones are depicted in Figure 8. Although the carbonyl group is contained in five- and six-membered rings, the vibrational situation is often quite different than for simple cyclohexanones and cyclopentanones. As such, the rules developed in this work are much more appropriate for investigating the effects of substitutions and conformations with respect to a specific polycyclic framework, rather than for making comparisons among the different frameworks. Nevertheless, the signs suggested by the projection diagrams are by and large consistent with the experimental $B(n-\pi^*)$ values found in the compounds investigated so far (Table IV and Figure 12). As a caveat, we discuss one exception. Undoubtedly, there are others.

On the basis of the projection diagram, one would expect a positive $B(n \rightarrow \pi^*)$ value for *trans*-1-decalone (**26**). Actually, $B(n-\pi^*, \mathbf{26})$ is slightly negative, -4×10^{-8}. In the present instance, this reduction in $B(n \rightarrow \pi^*)$ is likely caused by the suppression in amplitude of some pertinent vibrational modes due to the presence of the *B* ring of the decalone. However, since the basic molecular framework now belongs to C_1, it might be difficult to guess this unequivocally *a priori*. As implied above, it would be best to use the experimental $B(n-\pi^*, \mathbf{26})$ value as a zero of reference for making comparison among the *trans*-1-decalones.

IV. Experimental Section

The instrumentation used for MCD measurements and the special precautions taken as to the purity of the compounds have been described in detail elsewhere.[4] Solutions of formaldehyde in

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[30] (a) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 81, 3213 (1959); (b) H. Kim and W. D. Gwinn, *J. Chem. Phys.*, 51, 1815 (1969); (c) H. Howard-Lock and G. W. King, *J. Mol. Spectrosc.*, 36, 53 (1970).

hexane and in perfluorohexane (provided by Professor S. Lipsky, Department of Chemistry, University of Minnesota) were prepared by the thermal depolymerization of pure dry trioxymethylene as described by Cohen and Reid.[31] Since the rate of polymerization of formaldehyde in these solvents was relatively rapid, the optimum concentrations and scan speeds required for the necessary band resolution had to be determined by trial and error. Absorption and MCD measurements were carried out simultaneously using aliquots from the same solution. The spectra were measured at room temperature in cells of 1-cm path length. Cell blanks were obtained immediately following each sample measurement by replacing the solution with the appropriate solvent. The gelatinous polymer which was deposited on the cell windows during the time required for the measurement resulted in a decrease in the signal-to-noise but did not otherwise contribute significantly to the solution spectrum. Vibrational bands were more highly resolved in perfluorohexane than in hexane.

The MCD spectrum of dideuterioformaldehyde in perfluorohexane was also obtained. Although the vibrational bands were not as highly resolved as those of formaldehyde, the essential features observed in the MCD spectra of the two compounds are the same.

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[31] A. D. Cohen and C. Reid, *J. Chem. Phys.*, **24**, 85 (1956).

The Acid-Catalyzed Rearrangement of Camphor to 3,4-Dimethylacetophenone[1]

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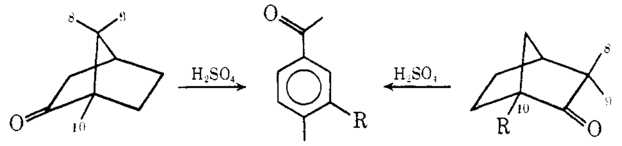
Abstract: The long known rearrangement of camphor to 3,4-dimethylacetophenone in concentrated sulfuric acid has been investigated using camphor-*8*-^{14}C and camphor-*9*-^{14}C. The results indicate that four interrelated rearrangement processes occur simultaneously, the two main pathways leading to 3,4-dimethylacetophenone (88–92 and 8–12%, respectively), *via* protonated fenchone as an intermediate. The other two processes occur within these main pathways, consisting of the internal racemizations of camphor (16%) and of a rearranged fenchone intermediate (2%).

The reaction of camphor (**1**) with concentrated sulfuric acid was first investigated in 1839, but it was not until 1893 that one of the reaction products was identified as 3,4-dimethylacetophenone (**2**),[3a] and not until 1901 that the other major product was shown to be carvenone.[3b] Fenchone (**3**) also gives 3,4-dimethylacetophenone (**2**) when treated with concentrated sulfuric acid,[4] and in 1950, Noyce[5] suggested a mechanism for this rearrangement, using as supportive evidence the fact that camphenilone (**4**) yields *p*-methylacetophenone (**5**) under similar conditions. The Noyce mechanism received further support from later work by Lutz and Roberts,[6] who studied the fenchone rearrangement using ^{14}C labeling in the *gem*-dimethyl groups. Noyce further proposed that fenchone is a likely intermediate in the conversion of camphor (**1**) to 3,4-dimethylacetophenone (**2**), a supposition also supported by Lutz and Roberts, who showed that under the reaction conditions fenchone and camphor are interconvertible. The latter authors further suggested a mechanism for this interconversion. By combining the proposed pathways one arrives at the mechanism shown in Chart I for the rearrangement of camphor to 3,4-dimethylacetophenone.[7]



1 **2**, R = CH_3 **3**, R = CH_3
5, R = H **4**, R = H

Lutz and Roberts comment on most of the steps in the mechanism, and their labeling experiments with fenchone-*8,9*-^{14}C support the suggested pathway from the intermediate **6** (protonated fenchone) to the final product **2**. In order to test further the proposed mechanism for the conversion of camphor to 3,4-dimethylacetophenone, we carried out the rearrangement of camphor-*8*-^{14}C and camphor-*9*-^{14}C by heating these compounds in concentrated sulfuric acid at 110° for 45 min. Under these conditions, very little camphor remained unreacted and the 3,4-dimethylacetophenone

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[1] Presented in part at the Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2–4, 1970. Taken from the dissertation of Robert J. Sysko submitted for the Doctor of Philosophy degree, University of Virginia, 1971.

[2] Recipient of a National Science Foundation Traineeship, 1967–1971.

[3] (a) H. E. Armstrong and F. S. Kipping, *J. Chem. Soc., London*, **63**, 75 (1893); (b) J. Bredt, F. Rochussen, and J. Monheim, *Justus Liebigs Ann. Chem.*, **314**, 369 (1901). A summary of the early investigations of the reaction of camphor with sulfuric acid can be found in these two papers.

[4] J. E. Marsh, *J. Chem. Soc., London*, **75**, 1058 (1899); H. E. Zaugg, *J. Amer. Chem. Soc.*, **67**, 1861 (1945).

[5] D. S. Noyce, *ibid.*, **72**, 924 (1950).

[6] R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962).

[7] For greater clarity classical carbonium ions, rather than their nonclassical counterparts, are used throughout this paper.