

Organic and Biological Chemistry

A Theory for the Quantitative Calculation of the Amplitudes of Cotton Effect Curves of Ketones^{1,2}

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Abstract: A theory has been derived, based on the one-electron approximation and utilizing the perturbation method, whereby the amplitude of the Cotton effect exhibited by the optical rotatory dispersion or circular dichroism curve of a ketone may be quantitatively calculated. Applications have been made to a number of alkylated cyclohexanones and reasonable agreement is found between theory and experiment. These optical properties were determined for a number of types of boat forms which have not been experimentally accessible for study.

It is well known that the $n \rightarrow \pi^*$ transition of a carbonyl group situated in an asymmetrical environment displays a Cotton effect, the sign and magnitude of which depend on the nature and position of the asymmetrical groups in the compound.³ A careful study of the rotatory dispersion curves of a vast variety of compounds and application of the available theory led to an empirical rule, the Octant rule,⁴ which can qualitatively predict the sign and magnitude of the Cotton effect of many molecules, and which has become of great use in the field of conformational analysis.⁵ In a few cases it has been possible to do quantitative empirical calculations, but only when an almost exact analogy is available from model compounds.⁶ When the asymmetrical groups in the carbonyl compound increase in number, and are situated in octants which give rise to Cotton effects of opposite sign, and particularly when they are of different kinds as in unsymmetrical boat forms, for example, it is often impossible to predict the sign of the resultant Cotton effect by the "Octant rule." It is therefore desirable to formulate a quantitative method which will account for the contribution of each individual group as a function of its nature and of its position relative to the carbonyl group. It is especially desirable to have a method for the calculation of the Cotton effect which can be applied to various types of

boat forms which are thought to exist in various molecules.

A more exact measure of the optical property of the $n \rightarrow \pi^*$ transition is the rotational strength (or rotatory strength), which is a measure of the area under the circular dichroism curve. If one makes the usual assumption that the observed circular dichroism curves of ketones are Gaussian shaped with identical half-band widths, it can then be shown that the sign and magnitude of the amplitude of the Cotton effect, as expressed in molecular rotation (molecular rotation equals specific rotation times molecular weight divided by 100), is almost directly proportional to the rotational strength (with the same proportionality constant) in the $n \rightarrow \pi^*$ transition of all ketones.³ Therefore, one can write $[A] = CR$ where $[A]$ and R are, respectively, the amplitude of the molecular rotation and the rotational strength, and C is the proportionality constant. It is known that R is the dot product of the electric moment $\bar{\mu}_e$ and the magnetic moment $\bar{\mu}_m$ ⁷ of the $n \rightarrow \pi^*$ transition. When the molecule is symmetrical, their dot product vanishes, since either $\bar{\mu}_e = 0$ or the two moments are perpendicular. Earlier attempts^{8,9} at calculating R for actual molecules proposed that in asymmetrical molecules the carbonyl group is perturbed by the group or groups causing the asymmetry, and some amount of 3d orbital is mixed into the π^* orbital. Since the transition from the n to the 3d orbital has a nonzero electric moment component in the direction of the magnetic moment (the direction of the C-O bond), the rotatory strength is no longer zero. The present work proposes a semiempirical method relating the overlaps between the perturbing orbital and the n and the π^* orbitals to the observed molecular rotation. The method is semiempirical in the sense that certain parameters have to be derived from known molecular rotations of compounds with known geometry. It is a perturbation method based on one-electron (Hückel)

(1) This is paper number L in the series "Conformational Analysis" (paper XLIX: N. L. Allinger, P. Crabbé, and G. Perez, *Tetrahedron*, in press) and paper number XII in the series "Organic Quantum Chemistry" (paper XI: N. L. Allinger, *Tetrahedron*, in press).

(2) This research was supported by Grant GP 4290 from the National Science Foundation.

(3) (a) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960; (b) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965; (c) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press Inc., New York, N. Y., 1965.

(4) W. Moffit, R. B. Woodward, A. Moscovitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

(5) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 161; (b) C. Djerassi, *Proc. Chem. Soc.*, 314 (1964); (c) C. Djerassi and W. Klyne, *J. Chem. Soc.*, 4929 (1962).

(6) (a) N. L. Allinger and M. A. DaRooge, *J. Am. Chem. Soc.*, **84**, 4561 (1962); (b) C. Djerassi, E. Lund, and A. A. Akhrem, *ibid.*, **84**, 1249 (1962).

(7) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, p 345.

(8) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

(9) A. Moscovitz, *Tetrahedron*, **13**, 48 (1961); *Advan. Chem. Phys.*, **4**, (1962).

theory, and gains both the advantages and disadvantages of those approximations.

Mathematical Derivation

The rotational strength R for a transition from state a to state b is written as

$$R = \vec{\mu}_e \cdot \vec{\mu}_m = \text{Im}[(a | \vec{R} | b) \cdot (b | \vec{M} | a)]$$

where

$$\vec{R} = e[ix + jy + kz] = e\vec{r}$$

and

$$\vec{M} = (e\hbar/2m_e c i) \left[i \left(\frac{y\partial}{\partial z} - \frac{z\partial}{\partial y} \right) + j \left(\frac{z\partial}{\partial x} - \frac{x\partial}{\partial z} \right) + k \left(\frac{x\partial}{\partial y} - \frac{y\partial}{\partial x} \right) \right] = (e\hbar/2m_e c i) (\vec{r} \times \vec{\nabla})$$

For the $n \rightarrow \pi^*$ transition of a carbonyl group perturbed by a neighboring group X, the rotational strength can be calculated as follows. The wave functions of the two states can be written as

$$a = n = C_C \pi_C + C_O \pi_O + C_n n_O + C_X X$$

and

$$b = \pi^* = C_C' \pi_C + C_O' \pi_O + C_n' n_O + C_X' X$$

where the C_i 's are the coefficients for the atomic orbitals (i) on carbon (C), oxygen (O and n), and of the perturbing group (X). The positions of the orbitals are shown in Figure 1.

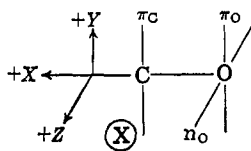


Figure 1.

It is assumed that the perturbation is small, hence in a , $C_n \gg C_X \gg C_C, C_O$, and in b , $C_C', C_O' \gg C_X' \gg C_n'$. Now

$$\vec{M} \pi_C = (e\hbar/2m_e c i) [-\pi_C(k)i + \pi_C(i)k]$$

$$\vec{M} \pi_O = (e\hbar/2m_e c i) [-\pi_O(k)i + \pi_O(i)k]$$

$$\vec{M} n_O = (e\hbar/2m_e c i) [n_O(j)i - n_O(i)j]$$

where $\pi_C(k)$ is the same wave function π rotated 90° from the original y direction to the z direction. In other words, the term y in the original wave function is replaced by z . The other terms have analogous meanings. We shall approximate X as spherically symmetrical,¹⁰ i.e., an s type wave function, then $\vec{M} X = 0$. We also obtain

$$(\pi^* | \vec{M} | n) = (e\hbar/2m_e c i) [-C_C C_n' S_{\pi_C(k)n_O} i - C_C C_X' S_{\pi_C(k)X} i + C_C C_X' S_{\pi_C(i)X} k - C_O C_n' S_{\pi_O(k)n_O} i - C_O C_X' S_{\pi_O(k)X} i + C_O C_X' S_{\pi_O(i)X} k + C_n C_C' S_{n_O(j)\pi_C} i + C_n C_O' S_{n_O(j)\pi_O} i + C_n C_X' S_{n_O(j)X} i - C_n C_X' S_{n_O(i)X} j] =$$

(10) Even if this is not a very good approximation for any particular X, the parameters describing X which are subsequently derived from experiment will tend to cancel out any error introduced by this approximation.

$$(e\hbar/2m_e c i) \{ [(-C_C C_n' + C_n C_C') S_{\pi_C(k)n_O} + (-C_O C_n' + C_n C_O') S_{\pi_O(k)n_O} - C_C C_X' S_{\pi_C(k)X} - C_O C_X' S_{\pi_O(k)X} + C_n C_X' S_{n_O(j)X} j - C_n C_X' S_{n_O(i)X} j + (C_C C_X' S_{\pi_C(i)X} + C_O C_X' S_{\pi_O(i)X}) k] \}$$

where S_{ij} is the overlap integral between orbitals i and j . When the overlap between X and the carbonyl group is small (< 0.1) most of the terms in the above expression can be neglected.¹¹ Thus it follows that

$$(\pi^* | M | n) \cong (e\hbar/2m_e c i) (C_n C_C' S_{\pi_C(k)n_O} + C_n C_O' S_{\pi_O(k)n_O}) i \cong C_M i$$

where

$$C_M \cong (e\hbar/2m_e c i) (C_n C_C' S_{\pi_C(k)n_O} + C_n C_O' S_{\pi_O(k)n_O})$$

and is a constant independent of the perturbing group X when the perturbation is small. To calculate the electric moment $(n | R | \pi^*)$, we write

$$n = C_\pi \pi^* + C_n n_O + C_X X$$

and

$$\pi^* = C_\pi' \pi^* + C_n' n_O + C_X' X$$

Hence

$$(n | \vec{R} | \pi^*) = e [C_\pi C_\pi' \vec{r}_{\pi^*} + C_n C_n' \vec{r}_{n_O} + C_X C_X' \vec{r}_X + (C_n C_X' + C_X C_n') \vec{G}_{\pi^* X} \cdot S_{\pi^* X} + (C_n C_X' + C_X C_n') \vec{G}_{nX} \cdot S_{nX}]$$

where $\vec{G}_{\pi^* X} = \int \pi^* X \vec{r} d\tau$, and $\vec{G}_{nX} = \int n X \vec{r} d\tau$. Taking the position of the oxygen atom O as origin, then $\vec{r}_{n_O} = 0$, also since $C_\pi C_X' \ll C_X C_n'$, and $C_X C_n' \ll C_n C_X'$, we can write

$$(n | \vec{R} | \pi^*) \cong e (C_\pi C_\pi' \vec{r}_{\pi^*} + C_X C_X' \vec{r}_X + C_X C_\pi' \vec{G}_{\pi^* X} S_{\pi^* X} + C_n C_X' \vec{G}_{nX} S_{nX}) \quad (1)$$

When the overlap between X and the carbonyl group is small, $C_\pi' \cong C_n \cong 1$. One needs now to estimate the values of C_π , C_X , and C_X' . These can be obtained by solving the determinant

$$\begin{vmatrix} \alpha_{\pi^*} - E & 0 & \beta_{\pi^* X} \\ 0 & \alpha_n - E & \beta_{nX} \\ \beta_{\pi^* X} & \beta_{nX} & \alpha_X - E \end{vmatrix} = 0$$

where the β 's are proportional to the S 's.

To a first-order approximation

$$C_X = \beta_{nX} / (\alpha_n - \alpha_X) \quad (2)$$

and

$$C_X' = \beta_{\pi^* X} / (\alpha_{\pi^*} - \alpha_X) \quad (3)$$

The perturbation by X causes the energy of state n to be raised from α_n to $[\alpha_n + \beta_{nX}^2 / (\alpha_n - \alpha_X)]$, hence

$$[\alpha_{\pi^*} - \alpha_n - \beta_{nX}^2 / (\alpha_n - \alpha_X)] C_\pi + \beta_{\pi^* X} C_X = 0$$

(11) This is due to the fact that the maximum values of the coefficients C_X and C_X' then will be of the order of 0.1 and those of C_C, C_O , and C_n' of the order of 0.02. Terms of the type $C_C C_X' S_{\pi_C(k)X}$ will at most be $0.02 \times 0.1 \times 0.1 = 0.0002$, and the $C_n C_X' S_{n_O(j)X}$ type will at most be $1 \times 0.1 \times 0.1 = 0.01$, compared to the value of $C_n C_C' S_{\pi_C(k)n_O}$ which is approximately $1 \times 0.8 \times 0.25 = 0.2$.

and

$$C_{\pi} = \frac{-\beta_{\pi^*X} \cdot \beta_{nX} / (\alpha_n - \alpha_X)}{\alpha_{\pi^*} - \alpha_n - \beta_{nX}^2 / (\alpha_n - \alpha_X)} = \frac{-\beta_{\pi^*X} \cdot \beta_{nX}}{(\alpha_{\pi^*} - \alpha_n)(\alpha_n - \alpha_X) - \beta_{nX}^2} \cong \frac{-\beta_{\pi^*X} \cdot \beta_{nX} / (\alpha_{\pi^*} - \alpha_n)(\alpha_n - \alpha_X)}{\beta_{nX}^2} \quad (4)$$

Substituting (2), (3), and (4) into (1), and setting $C_{\pi'}$ and C_n equal to 1, one obtains

$$(n|\vec{R}|\pi^*) \cong e \left[\frac{-\beta_{\pi^*X} \cdot \beta_{nX}}{(\alpha_{\pi^*} - \alpha_n)(\alpha_n - \alpha_X)} \vec{r}_{\pi^*} + \frac{\beta_{nX} \cdot \beta_{\pi^*X}}{(\alpha_n - \alpha_X)(\alpha_{\pi^*} - \alpha_X)} \vec{r}_X + \beta_{nX} \vec{G}_{\pi^*X} S_{\pi^*X} / (\alpha_n - \alpha_X) + \beta_{\pi^*X} \vec{G}_{nX} S_{nX} / (\alpha_{\pi^*} - \alpha_X) \right] \quad (5)$$

Since only the x component of the moment is of interest, vectors of the type \vec{r}_{π^*} will be written as $r_{\pi^*}i$, where r_{π^*} is the x component of \vec{r}_{π^*} . Defining $(\alpha_{\pi^*} - \alpha_n)/r_{\pi^*} = k$

$$\alpha_n - \alpha_X = k_{1X}$$

$$\alpha_{\pi^*} - \alpha_X = k_{2X}$$

$$\beta_{nX} = k_{3X} S_{nX}$$

$$\beta_{\pi^*X} = k_{4X} S_{\pi^*X}$$

$$\vec{G}_{\pi^*X} = C_{1X} r_X$$

and

$$G_{nX} = C_{2X} r_X \quad (6)$$

where k is a constant independent of the nature of X , and k_{1X} , k_{2X} , k_{3X} , k_{4X} , C_{1X} , and C_{2X} are constants dependent on the nature of X .

Substituting (6) into (5)

$$(n|\vec{R}|\pi^*)_{x \text{ component}} = e(-k_{3X}k_{4X}S_{nX}S_{\pi^*X}/kk_{1X} + k_{3X}k_{4X}S_{nX}S_{\pi^*X}r_X/k_{1X}k_{2X} + k_{3X}S_{nX}S_{\pi^*X}k_{2X}C_{1X}r_X/k_{1X}k_{2X} + k_{4X}S_{\pi^*X}S_{nX}k_{1X}C_{2X}r_X/k_{1X}k_{2X})i = eS_{nX}S_{\pi^*X}[-k_{3X}k_{4X}/kk_{1X} + (k_{3X}k_{4X} + k_{2X}k_{3X}C_{1X} + k_{1X}k_{4X}C_{2X})r_X/k_{1X}k_{2X}]i$$

Letting $k_{3X}k_{4X}/kk_{1X} = C_X$, and $(k_{3X}k_{4X} + k_{2X}k_{3X}C_{1X} + k_{1X}k_{4X}C_{2X})/k_{1X}k_{2X} = C_X'$, one obtains

$$(n|\vec{R}|\pi^*) = eS_{nX}S_{\pi^*X}C_X(C_X'r_X - 1)i$$

Therefore the rotatory strength (R) of the transition perturbed by the group X is equal to

$$R = eC_M C_X S_{nX} S_{\pi^*X} (C_X' r_X - 1)$$

Since

$$[A] = CR$$

$$[A] = k_X S_{nX} S_{\pi^*X} (k_X' x_X - 1) \quad (7)$$

where $k_X = eC_M C_X C$, $k_X' = C_X'$, and $x = r$.

Method of Calculation

From eq 7, one sees that there are two constants, k_X and k_X' , to be evaluated for each perturbing group X . In this work only the effect of the methyl group will be considered, although the method can be extended to

any type of X . However, in any compound containing hydrogens and one or more methyl group substituents, the observed optical rotation results from the difference between the methyl groups and the corresponding hydrogen atoms. For example, in α -axial methylcyclohexanone, the observed molecular rotation is the difference between the molecular rotation caused by the α -axial methyl group and that caused by the α -axial hydrogen. Expressed in mathematical form

$$[A] = k_{Me} S_{nMe} S_{\pi^*Me} (k_{Me}' x_{Me} - 1) - k_H S_{nH} S_{\pi^*H} (k_H' x_H - 1) \quad (8)$$

In actual fact, then, there are four constants to be evaluated, requiring the values of the molecular rotation of four compounds of known geometry.

Geometry. Since all the compounds dealt with in the present work are derivatives of cyclohexanone, it is important to obtain the geometry of the ring itself and of its substituents as accurately as possible. This was done for the cyclohexanone in its usual chair form, and also for the series of boat forms which are obtained by pseudo-rotation, where the pseudo-rotational parameter¹² (θ) has the value of 0° , $\pm 60^\circ$, and $\pm 90^\circ$. In the chair form (Figure 2), $\angle C_2C_1C_6$ is taken to be

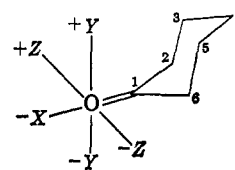


Figure 2.

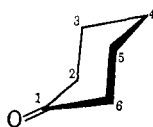
116° , R_{12}, R_{16} to be 1.500 A, and R_{CO} to be 1.220 A. The rest of the molecule assumes the cyclohexane geometry, *i.e.*, bond length of 1.530 A and bond angles of 111.6° .¹³ Any substituent S is assumed to be situated at a position such that $\angle SCC = 109^\circ 28'$. This results in $\angle SCH = 107^\circ 17'$, a quite reasonable figure.¹⁴ When the substituent is a methyl group, the three C-H bonds of the methyl group always assume a staggered position relative to the ring. The C-H and C-C bond lengths of the methyl group are taken to be 1.10 and 1.5398 A, respectively.¹⁵ Exactly the same data were used to evaluate the geometries of the boat forms, except the boats with $\theta = 60$ and 90° . In these cases, conditions imposed on the other parts of the molecule force the $C_3C_4C_5$ angle to be 114.2° instead of 111.6° . In all cases, O, C_1 , and C_2 are placed on the x - y plane, O being the origin and C_2 having a positive y coordinate; all other ring carbon atoms have positive z coordinates. On any given ring carbon atom, the substituent having the smaller absolute value for the z coordinate is called equatorial, and the other axial. The coordinates of the ring carbons and their equatorial and axial substituents of the chair and various boat forms are given in the Tables I-IV. The three atoms attached to a common methyl carbon are numbered

(12) For definition, see N. L. Allinger, J. Allinger, and M. A. Darroge, *J. Am. Chem. Soc.*, **86**, 4061 (1964).

(13) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

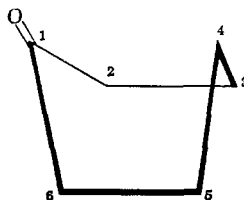
(14) Compared with the geometry of propane where $\angle CCC = 112.4^\circ$, $\angle HCH = 106.1^\circ$, $R_{CH} = 1.096$ A.: see D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

(15) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

Table I. Geometry of the Cyclohexanone Ring, Chair Form^a

Ring carbon	Coordinates, A	Substituents ^b	
		Equatorial	Axial
1	$x = 1.22$ $y = 0$ $z = 0$		
2	$x = 2.01488$ $y = 1.27208$ $z = 0$	$2.01488 - 0.61390D$ $1.27208 + 0.77658D$ $0.14153D$	$2.01488 + 0.43280D$ $1.27208 + 0.12254D$ $-0.89314D$
3	$x = 3.08838$ $y = 1.26543$ $z = 1.09017$	$3.08838 + 0.58490D$ $1.26543 + 0.80446D$ $1.09017 - 0.10333D$	$3.08838 - 0.43617D$ $1.26543 + 0.06336D$ $1.09017 + 0.89760D$
4	$x = 3.94614$ $y = 0$ $z = 1.02825$	$3.94614 + 0.53338D$ 0 $1.02825 - 0.84588D$	$3.94614 + 0.64934D$ 0 $1.02825 + 0.76050D$
5	$x = 3.08838$ $y = -1.26543$ $z = 1.09017$	$3.08838 + 0.58490D$ $-1.26543 - 0.80446D$ $1.09017 - 0.10333D$	$3.08838 - 0.43617D$ $-1.26543 - 0.06336D$ $1.09017 + 0.89760D$
6	$x = 2.01488$ $y = -1.27208$ $z = 0$	$2.01488 - 0.61390D$ $-1.27208 - 0.77658D$ $0.14153D$	$2.01488 + 0.43280D$ $-1.27208 - 0.12254D$ $-0.89314D$

^a $R_{12} = R_{16} = 1.50$ A, all other bond lengths = 1.53 A. $\angle C_2C_1C_6 = 116^\circ$; all other angles = 111.6° . ^b The distance from the substituent to the attached ring carbon atom is D , A.

Table II. Geometry of the Cyclohexanone Ring, Boat Form, $\theta = 0^\circ$ ^a

Ring Carbon	Coordinates, A	Substituents ^b	
		Equatorial	Axial
1	$x = 1.22$ $y = 0$ $z = 0$		
2	$x = 2.01488$ $y = 1.27208$ $z = 0$	$2.01488 - 0.61390D$ $1.27208 + 0.77658D$ $0.14153D$	$2.01488 + 0.43280D$ $1.27208 + 0.12254D$ $-0.89314D$
3	$x = 3.08838$ $y = 1.26543$ $z = 1.09017$	$3.08838 + 0.90424D$ $1.26543 + 0.06334D$ $1.09017 - 0.42231D$	$3.08838 - 0.11235D$ $1.26543 + 0.80448D$ $1.09017 + 0.58326D$
4	$x = 3.01324$ $y = 0$ $z = 1.94688$		
5	$x = 3.08838$ $y = -1.26543$ $z = 1.09017$	$3.08838 + 0.90424D$ $-1.26543 - 0.06334D$ $1.09017 - 0.42231D$	$3.08838 - 0.11235D$ $-1.26543 - 0.80448D$ $1.09017 + 0.58326D$
6	$x = 2.01488$ $y = -1.27208$ $z = 0$	$2.01488 - 0.61390D$ $-1.27208 - 0.77658D$ $0.14153D$	$2.01488 + 0.43280D$ $-1.27208 - 0.12254D$ $-0.89314D$

^a $R_{12} = R_{16} = 1.50$ A; all other bond lengths = 1.53 A. $\angle C_2C_1C_6 = 116^\circ$; all other angles = 111.6° . ^b The distance from the substituent to the attached ring carbon atom is D , A.

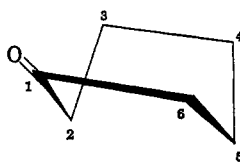
1, 2, and 3 in the order of the increasing magnitudes of their x coordinates. For example, the three hydrogen atoms of the 2-equatorial methyl group having coordinates (0.009, 2.493, -0.898), (0.374, 2.329, 1.584), and (1.882, 3.775, 0.185) are designated as 2eH1, 2eH2, and 2eH3, respectively.

When the compound consists of more than one ring, the positions of the atoms on the rings other than the one containing the carbonyl group are approximated as

substituents of the cyclohexanone ring. Thus in 1-decalone for example, the positions of the carbon atoms 8, 7, 6, 5, and the methyl group are approximated as those of 6eC, 6eC3, 5eC1, 5eC, and 5aC, respectively.

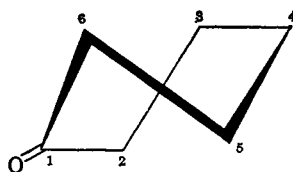
Evaluation of Constants. From an independent work on the calculation of the electronic spectrum of acetone,¹⁶ we arrived at the wave function of the π^* and n orbitals as $\pi^* = -0.896C_\pi + 0.444O_\pi$ and $n =$

(16) J. C. Tai and N. L. Allinger, unpublished.

Table III. Geometry of the Cyclohexanone Ring, Boat Form, $\theta = 60^\circ$ ^a

Ring carbon	Coordinates, A	Substituents ^b	
		Equatorial	Axial
1	$x = 1.22$ $y = 0$ $z = 0$		
2	$x = 2.01488$ $y = 1.27208$ $z = 0$	$2.01488 - 0.61390D$ $1.27208 + 0.77658D$ $0.14153D$	$2.01488 + 0.43280D$ $1.27208 + 0.12254D$ $-0.89314D$
3	$x = 3.06840$ $y = 1.27791$ $z = 1.10949$	$3.06840 + 0.60118D$ $1.27791 + 0.78968D$ $1.10949 - 0.12245D$	$3.06840 - 0.41558D$ $1.27791 + 0.15509D$ $1.10949 + 0.89624D$
4	$x = 3.90959$ $y = 0$ $z = 1.09414$	$3.90959 + 0.97287D$ $0.21765D$ $1.09414 - 0.07840D$	$3.90959 - 0.08131D$ $-0.44182D$ $1.09414 + 0.89341D$
5	$x = 3.51974$ $y = -0.99588$ $z = 0$	$3.51974 + 0.49618D$ $-0.99588 - 0.85735D$ $0.13697D$	$3.51974 + 0.27198D$ $-0.99588 + 0.36421D$ $-0.89072D$
6	$x = 2.01488$ $y = -1.27208$ $z = 0$	$2.01488 - 0.23926D$ $-1.27208 - 0.54248D$ $-0.80528D$	$2.01488 - 0.23926D$ $-1.27208 - 0.54248D$ $0.80528D$

^a $R_{12} = R_{16} = 1.50$ A; all other bond lengths = 1.53 A. $\angle C_2C_1C_6 = 116^\circ$, $\angle C_3C_4C_5 = 114.2^\circ$; all other angles = 111.6° . ^b The distance from the substituent to the attached ring carbon atom is D , A.

Table IV. Geometry of the Cyclohexanone Ring, Boat Form, $\theta = 90^\circ$ ^a

Ring carbon	Coordinates, A	Substituents ^b	
		Equatorial	Axial
1	$x = 1.22$ $y = 0$ $z = 0$		
2	$x = 2.01488$ $y = 1.27208$ $z = 0$	$2.01488 - 0.51593D$ $1.27208 + 0.71536D$ $0.47124D$	$2.01488 + 0.13941D$ $1.27208 + 0.30586D$ $-0.94182D$
3	$x = 3.37180$ $y = 1.08331$ $z = 0.68257$	$3.37180 + 0.50253D$ $1.08331 + 0.86434D$ $0.68257 - 0.01929D$	$3.37180 - 0.13997D$ $1.08331 - 0.24074D$ $0.68257 + 0.96044D$
4	$x = 4.20282$ $y = 0$ $z = 0$	$4.20282 + 0.61357D$ $0.41956D$ $-0.66896D$	$4.20282 + 0.61357D$ $-0.41956D$ $0.66896D$
5	$x = 3.37180$ $y = -1.08331$ $z = -0.68257$	$3.37180 + 0.50253D$ $-1.08331 - 0.86434D$ $-0.68257 + 0.01929D$	$3.37180 - 0.13997D$ $-1.08331 + 0.24074D$ $-0.68257 - 0.96044D$
6	$x = 2.01488$ $y = -1.27208$ $z = 0$	$2.01488 - 0.51593D$ $-1.27208 - 0.71536D$ $-0.47124D$	$2.01488 + 0.13941D$ $-1.27208 - 0.03586D$ $0.94182D$

^a $R_{12} = R_{16} = 1.50$ A; all other bond lengths = 1.53 A. $\angle C_2C_1C_6 = 116^\circ$, $\angle C_3C_4C_5 = 114.2^\circ$; all other angles = 111.6° . ^b The distance from the substituent to the attached ring carbon atom is D , A.

O_n , where C_n , O_n , and O_n are Slater-type wave functions with $Z_c = 2.938$, and $Z_o = 4.431$. These numbers were used in the preliminary calculations of the present work. The hydrogen wave function is $1s$ with $Z = 1$. The main problem remaining at this point was to choose a simple orbital to approximate the methyl group, and it was decided to pick a $2s$ orbital with an effective nuclear charge Z_c , the value of the latter to be chosen. A computer program was written, which,

with the x, y, z coordinates of a substituent as input, would calculate the overlap between the substituent and the π^* and the n orbitals, the substituent being treated as an ns orbital with orbital exponent δ , where $n = 1, 2, 3$, or 5 . The formulas used for calculating the overlap integrals between the ns and $2p$ orbitals were taken from the literature.¹⁷ The known molecular

(17) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

amplitudes of α -axial, α -equatorial, β -axial, and β -equatorial methylcyclohexanones were used to evaluate the four constants mentioned above. After a few trials it became apparent that with the use of Slater-type wave functions the overlap decreased too rapidly with distance, resulting in much smaller rotations calculated for remote groups than were observed, unless the hydrogen atoms exerted an unreasonably large effect. We therefore turned to SCF wave functions of carbon and oxygen expressed as linear combinations of Slater wave functions¹⁸ $\bar{\psi} = \sum_i C_i \psi_i$. Corresponding to $Z_c = 2.938$, and $Z_o = 4.431$, the 2p orbitals for carbon and oxygen are

$$\bar{\psi}_c = 0.31916\psi_c(0.84720) + 0.50063\psi_c(1.27890) + 0.25045\psi_c(2.30930) + 0.01097\psi_c(5.69710)$$

$$\bar{\psi}_o = 0.13324\psi_o(1.03480) + 0.60066\psi_o(1.69500) + 0.34397\psi_o(3.33040) + 0.01500\psi_o(7.68267)$$

where the numbers in parentheses are the orbital exponents of the basis p functions.

It is noted that with the use of the SCF wave functions, the coefficients in the π^* orbital (-0.896 and 0.444) no longer have their original meanings. The data presented below are based on the use of such orbitals for π_{CO}^* and n_O , together with $1s(1)$ orbitals for hydrogens and $2s(0.47)$ orbitals for methyl carbons. (The value of 0.47 for the exponent was chosen to fit as well as possible the four standard compounds mentioned.) A survey of the overlap integrals shows that the effect of a hydrogen atom is negligible when its distance from the carbonyl carbon is more than $5A$. The effect of a methyl group becomes insignificant at distances larger than $7A$.

It was found that very small variances in the molecular rotation values of any of the four standard compounds resulted in large changes in the relative importance of the H and C contributions to the rotation. Since hydrogen inclusion complicates the problem considerably, and since we have not so far been able to assign any hydrogen contribution such as to bring the calculated values into better agreement with experiment, we shall present the results based on the neglect of any hydrogen contribution to the molecular rotation of these compounds. Thus eq 8 reduces to

$$[A] = k_{Me} S_{n_{Me}} S_{\pi^*_{Me}} (k'_{Me} x_{Me} - 1) \quad (9)$$

Results and Discussion

The molecular amplitudes of a number of available compounds of known geometry were calculated assuming $[A]_H = 0$, $k_{Me} = -3200$ deg/mole, and $k'_{Me} = 4.5 A^{-1}$. The calculated values are compared with the experimental values in Table V. In many cases where experimental rotational strengths are given in the literature, they were converted to molecular amplitudes by multiplication by 15.1×10^{40} . This factor is based on the room-temperature Cotton effect measurement and circular dichroism measurement of 3-equatorial methylcyclohexanone. The former gives a molecular amplitude of 25° , the latter, a rotational strength of 1.65×10^{-40} cgs unit. The amplitude of the rotation for the cyclohexanone ring in chair and

(18) E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

boat forms $\theta = 0, 60,$ and 90° , and the effect of methyl substitution at many positions were also calculated. The results are presented in Tables VI-IX.

This method gives the same prediction regarding the sign of the Cotton effect as the older qualitative method (the octant rule).¹⁹ Both methods predict the $z = 0$ and $y = 0$ planes as two of the three planes which divide the molecular environment of the carbonyl group into eight spatial regions. The third plane which divides the "front" and "rear" octants, however, is situated differently. Since k'_{Me} has a value of 4.5 , it can be seen from eq 9 that when x has the value 0.22 , the term $(k'_{Me} x_{Me} - 1)$ changes sign. For methyl substituents, therefore, the present theory predicts the plane $x = 0.22$ is the third plane which divides front and rear octants, while the original version of the octant rule divides these octants at the nodal surface of the carbonyl π^* orbital, and is invariant with the nature of the substituents.

Generally speaking, the agreement between the calculated and observed amplitudes is good. The experimental data are somewhat variable as to reliability for a number of reasons; perhaps the fundamentally most serious difficulty is that there appears to be a variable and unpredictable effect from solvation,²⁰ which appears to be minimal in EPA, and to which solvent we refer when possible.

The calculated rotational amplitudes for the simple monomethylcyclohexanones agree with the experimental values to within the limits of experimental error, except that no direct measurement of the 3-axial methyl value is available. The observed value was calculated from the experimental data in a roundabout way, as follows. Independent measurements have given values for the conformational free energy of β -methylcyclohexanone of 1.4^{21} and 1.8^{22} kcal/mole. If the molecular amplitude of the compound is taken as being due completely to the equatorial conformer at -192° , then from the observed amplitude at room temperature, the amplitude of the axial conformer can be calculated. From the two free-energy values cited, the two molecular amplitudes calculated for the axial conformer are 33 and 96. We have picked an intermediate value (55) for the quantity in question, which seems to fit reasonably well with the available data.

If we consider compounds which may reasonably be assumed to be completely in the chair form, the most serious discrepancies between the calculated and experimental amplitudes occur with the α -axial isopropyl and the β -equatorial *t*-butylcyclohexanones. If one considers the changes which will result when methyl groups in the corresponding compounds are converted to these more complicated alkyl groups, it is clear that the present theory will demand the observed qualitative changes. There do not appear to be possible any small changes in parameters which will noticeably

(19) The signs of the wave functions for the various lobes of the n and π^* orbitals assure this will be true, and hence the multiplication of the signs of the coordinates of a substituent (if the molecule is properly oriented in the coordinate system) will give the qualitative Cotton effect curve. See ref 5a, p 165.

(20) (a) N. L. Allinger, J. G. D. Carpenter, and M. A. DaRooge, *J. Org. Chem.*, **30**, 1423 (1965); (b) A. Moscovitz, K. M. Wellman, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **50**, 799 (1963).

(21) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **84**, 2201 (1962).

(22) B. Rickborn, *ibid.*, **84**, 2414 (1962).

Table V. Molecular Amplitudes of Some Saturated Ketones

Compound	[A] ^r		Ref
	Calcd	Obsd ^a	
[R]-A axial methylcyclohexanone	-71	-67	a
[S]-Equatorial methylcyclohexanone	+9	+9	a
[S]-Axial methylcyclohexanone	+66	+(31-93)	b
[R]-Equatorial methylcyclohexanone	+26	+25, +33 (-192°)	c,d
[S]-A axial isopropylcyclohexanone	-172	-98, -95	e,f
[R]-2-Equatorial <i>t</i> -butylcyclohexanone	+29	+(33-39)	g
[R]-2-Equatorial isopropylcyclohexanone	+22, ^h +21 ⁱ	+35, +48 (-192°) +(15-21), +19 (-192°)	f e,f
[R]-3-Equatorial <i>t</i> -butylcyclohexanone	+52	+33 (-192°)	d
5 α -Cholestan-3-one	+42	+(38-58)	j
5 α -Methylcholestan-3-one	+108	+73	c
10-Methyl- <i>trans</i> -2-decalone	+48	+47	k
Coprostanone	-18	-23	l
D-Homoandrostan-17a-one	+3	0	p
17 α -Methyl-D-homoandrostan-17a-one	-6	0	p
1 β -Methyl-5 α -dihydrotestosterone	+14 (chair form) -24 (boat, $\theta = 0^\circ$) +96 (boat, $\theta = 60^\circ$)	+82, +86 (-192°)	f
1 α -Methyl-5 α -dihydrotestosterone	-26 (chair form) -75 (boat, $\theta = 0^\circ$) +52 (boat, $\theta = 60^\circ$)	+42, +55 (-192°)	f
17 β -Methyl-D-homoandrostan-17a-one	+74 (chair form) +109 (boat, $\theta = 60^\circ$) +107 (boat, $\theta = -60^\circ$) +106 (boat, $\theta = 90^\circ$)	+(112-159)	m
17,17-Dimethyl-D-homoandrostan-17a-one	+65 (chair form) +38 (boat, $\theta = 60^\circ$) +43 (boat, $\theta = -60^\circ$) +27 (boat, $\theta = 90^\circ$)	-46	n
Cholestan-1-one	+4 (chair) -50 (boat, $\theta = -60^\circ$) -96 (boat, $\theta = 120^\circ$) -75 (boat, $\theta = 90^\circ$)	...	o

^a C. Beard, C. Djerassi, J. Sicher, F. Sipos, and M. Tichy, *Tetrahedron*, **19**, 919 (1963). ^b The rotation is estimated from the rotational strength at 25 and -192° of the 3-axial methyl group, and the axial-equatorial inversion energy. See text. ^c C. Djerassi and G. W. Krakower, *J. Am. Chem. Soc.*, **81**, 237 (1959); C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963). ^d K. W. Wellman, E. Bunnberg, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 1870 (1963). ^e C. Djerassi, P. A. Hart, and C. Beard, *ibid.*, **86**, 85 (1964). ^f K. M. Wellman, W. S. Briggs, and C. Djerassi, *ibid.*, **87**, 73 (1965). ^g C. Djerassi, P. A. Hart, and C. J. Warawa, *ibid.*, **86**, 78 (1964). ^h The isopropyl group is made by replacing the 2eH2 and 2eH3 atoms with methyl groups. ⁱ The isopropyl is made by replacing 2eH1 and 2eH3 atoms with methyls. ^j [A] = 48-55 measured in methanol: C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963); [A] = +38 measured in cyclohexane, [A] = +46, measured in dioxane: ref 20a; [A] = 48 measured in dioxane: C. S. Barns and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1962 (1962). ^k C. S. Barns and C. Djerassi, *ibid.*, **84**, 1962 (1962). ^l C. Djerassi and W. Closson, *ibid.*, **78**, 3761 (1956). ^m The value reported earlier (C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1093 (1962)) was +159, but a recent determination with more accurate equipment gave +112: W. Klyne, personal communication. Whether the latter is a more accurate value or the result of epimerization of the sample on prolonged standing is uncertain. The value of -46 for the dimethyl compound has been checked and confirmed with the original sample. ⁿ M. Uskovic, M. Gut, E. N. Trachtenberg, W. Klyne, and R. I. Dorfman, *J. Am. Chem. Soc.*, **82**, 4965 (1960). ^o K. M. Wellman, R. Records, E. Bunnberg, and C. Djerassi, *ibid.*, **86**, 492 (1964). ^p See the reference given in footnote m. ^q Temperatures are at or near 25° unless otherwise specified. ^r The symbol [A] for the amplitude of an ORD curve was introduced in ref 4, and we use the quantity herein according to their definition. Other workers use a^{3b} or a^{3c} to mean the same thing.

improve the fit for these two compounds, without affecting serious changes in the calculated values for the corresponding methyl compounds. Our feeling is, therefore, that the difficulty with these two compounds rests largely with the model on which the calculations are based. There may, for example, be deformations or boat forms which are unaccounted for, or the α -axial isopropyl compound may well suffer from asymmetric solvation to an unusual degree.

Potential tests of the accuracy of the predictions are boat forms, but conformationally pure compounds which are known to be completely in the boat forms are quite rare, and the pseudo-rotational conformations of the boats further complicate the problem. Compounds which do or might include the desired characteristics are the 1-methyl-5 α -dihydrotestosterones, 1-cholestanone, and the D-homo-17 α -keto steroids methylated at C-17.

Each of these can be considered in some detail, as some experimental data are available for comparison.

Taking the 1-methyl-5 α -dihydrotestosterones first, the experimental amplitudes are as given in Table V. The 1 β -methyl compound has [A] = +86 at -192° , and this number is almost invariant with temperature. The β -methyl and C-11 exhibit what amounts to a *syn*-diaxial dimethyl interaction (3.7 kcal/mole)²³ if ring A is in the chair form. Actually, the *syn*-diaxial dimethyl interaction energy is as low as it is because of extensive bond deformation which occurs in a monocyclic system.²⁴ Such deformation is more difficult here because C-12 is more rigidly held. The figure, 3.7 kcal/mole, is therefore a minimum of energy; the actual value may be very much larger. If ring A assumes a boat form to alleviate this interaction, it is clear that the boat with $\theta = 60^\circ$ is unfavorable, because 1 β -methyl, C-1, C-10, and C-19 constitute an eclipsed butane unit.

(23) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

(24) B. Waegell, P. Pouzet, and G. Ourisson, *Bull. Soc. Chim. France*, 1821 (1963).

Table VI. Molecular Rotations of Methyl-Substituted Cyclohexanones in the Chair Form

Position of methyl group	Calculated change in [A] by introduction of group
2-Equatorial	+9
2-Axial	-71
3-Equatorial	+26
3-Axial	+66
4-Equatorial	0
4-Axial	0
2-Equatorial Me 1	+7
2-Equatorial Me 2	+8
2-Equatorial Me 3	+5
2-Axial Me 1	-61
2-Axial Me 2	-40
2-Axial Me 3	-13
3-Equatorial Me 1	+20
3-Equatorial Me 2	-8
3-Equatorial Me 3	+14
3-Axial Me 1	+7
3-Axial Me 2	+47
3-Axial Me 3	+24
4-Equatorial Me 1	0
4-Equatorial Me 2	+2
4-Equatorial Me 3	-2
4-Axial Me 1	0
4-Axial Me 2	-6
4-Axial Me 3	+6

Table VII. Molecular Amplitudes Calculated for Methylcyclohexanones in the Boat Form, $\theta = 0^\circ$

Compound	[A], calcd
Cyclohexanone	0
2-Equatorial methylcyclohexanone	+9
2-Axial methylcyclohexanone	-71
3-Equatorial methylcyclohexanone	+9
3-Axial methylcyclohexanone	+61

Table VIII. Molecular Amplitudes Calculated for Methylcyclohexanones in the Boat Form, $\theta = 60^\circ$

Compound	[A], calcd	$\Delta[A]^a$
Cyclohexanone	+52	...
2-Equatorial methylcyclohexanone	+61	+9
2-Axial methylcyclohexanone	-19	-71
3-Equatorial methylcyclohexanone	+76	+24
3-Axial methylcyclohexanone	+120	+68
4-Equatorial methylcyclohexanone	+54	+2
4-Axial methylcyclohexanone	+29	-23
5-Equatorial methylcyclohexanone	+46	-6
5-Axial methylcyclohexanone	+67	+15
6-Equatorial methylcyclohexanone	+116	+64
6-Axial methylcyclohexanone	-12	-64

^a $\Delta[A]$ is the change from the cyclohexanone value by the substitution of a H by a methyl group at the indicated position.

On the other hand, the original offending interaction is not relieved if $\theta = 0^\circ$. Only near $\theta = 30^\circ$ is there hope of finding a boat form of reasonably low energy. (The value calculated from previous data¹² is 8.6 kcal, or 3.1 kcal above that of the chair.) Since the lack of energy lowering by deformation of the chair form may raise its energy by more than 3 kcal, no prediction can be

Table IX. Molecular Amplitude Calculated for Methylcyclohexanones in the Boat Form, $\theta = 90^\circ$

Compound	[A], calcd	$\Delta[A]^a$
Cyclohexanone	+58	...
2-Equatorial methylcyclohexanone	+90	+32
2-Axial methylcyclohexanone	-21	-79
3-Equatorial methylcyclohexanone	+76	+18
3-Axial methylcyclohexanone	+96	+38
4-Equatorial methylcyclohexanone	+52	-6
4-Axial methylcyclohexanone	+52	-6
5-Equatorial methylcyclohexanone	+76	+18
5-Axial methylcyclohexanone	+96	+38
6-Equatorial methylcyclohexane	+90	+32
6-Axial methylcyclohexanone	-21	-79

^a $\Delta[A]$ is the change from the cyclohexanone value by the substitution of an H by a methyl group at the indicated position.

made from energetics as to which alternative is preferable. The amplitude of the Cotton effect of the 1β -methyl derivative is more positive than that of the unmethylated compound, whereas the methyl is in a negative octant if the ring is in a chair form. Clearly some unusual conformation is present, and a boat form with $\theta \approx 30^\circ$ seems the only reasonable possibility. The amplitudes predicted by the present work for the boats with $\theta = 0$ to 60° would be from -24 to +96, and the experimental value indicates that something nearer the latter is more likely. Since the value calculated for the chair is +14, the lack of variation of [A] with temperature means there is essentially none of the chair form in equilibrium with the boat, and indicates the interaction in the chair form is much more severe than the simple model compound would indicate.²⁵

Next the 1α -methyl compound was considered. Here the methyl is engaged in three unfavorable interactions in the chair form, which total 2.2 kcal/mole judging from simple (more flexible) models, plus the energy of the ring system itself (1.8 kcal/mole). The boat form with $\theta = 0^\circ$ lowers this value to 1.7 kcal/mole, but at the cost of two eclipsed ethanes, so it will not occur to any extent at room temperature. If $\theta = 60^\circ$, there are very serious interactions of the methyl with C-9 and C-11 which are prohibitively large. At about $\theta = 30^\circ$, the interaction with C-11 is reduced to about 0.4 kcal/mole, that with C-9 is 3.9 kcal/mole, and the ring energy is about 3.8 kcal/mole. The energy of the boat is then 8.1 kcal/mole, compared to 4.0 kcal/mole for the chair. Thus the chair is predicted to be more favorable, but since the models on which this prediction is based are more flexible than the system considered here, the prediction is of questionable reliability. The amplitudes predicted are: chair, -26, boats; $\theta = 0^\circ$, -75, and $\theta = 60^\circ$, +52. The observed amplitude is +55 at -192° which demands a boat form, and it decreases to +42 at 25° , which could be a result of the pseudo-rotation of the boat taking a lower effective θ , or it could result from mixing in a rather small amount of chair form.

The 5α -methylcholestan-3-one is calculated to have a strong positive curve ([A] = +108) for the chair-form,

(25) From a study of the nmr spectrum (W. J. Wechter, G. Slomp, F. A. MacKellar, R. Wiechert, and U. Kerb, *Tetrahedron*, 21, 1625 (1965)), the A ring in this compound was assigned a boat form with θ near 30° . They presumed the 1α -methyl derivative had a normal chair conformation, and apparently did not investigate other possibilities.

and similar curves ($[A] = +40$ to $+70$) for boat forms. The lack of change of $[A]$ with temperature may simply result from the conformations present having rotations which are too similar for small changes in composition to be evident.

The D-homo-17 α -ketoandrostanes methylated at C-17 are compounds long thought to possess boat forms in ring D.²⁶ It has been suggested on the basis of conformational analysis that the form with $\theta = 90^\circ$ should exist for the *gem*-dimethyl compound, while θ should be reduced somewhat for the 17 β -methyl. Calculated values for $\theta = 60, -60,$ and 90° are $+38, +43,$ and $+27$ for the dimethyl, and $+109, +107,$ and $+106$ for the monomethyl. The observed values are -46 and $+(112-159)$. For the latter the agreement is satisfactory considering the experimental uncertainty. The synthesis of the dimethyl compound should be repeated and the rotation rechecked.

The agreement between the calculated and found

(26) See ref 12, and references therein.

values for the molecular amplitudes of the compounds listed in Table V is good in a majority of the cases. The theory appears to give reliable predictions as long as certain conditions are met. The most important condition is that the solvation effects be the same in the compounds in question as they were in the model compounds from which the parameters for the calculations were deduced. Because the solvation effects are so poorly understood at present, this appears to be the most serious limitation for the calculation of these quantities. Limitations in the theory itself result from the fact that it was developed by perturbation methods. Hence there should be smaller percentage errors when the substituents being studied are farther from the carbonyl group. The percentage errors can become quite large when the substituents are near nodal surfaces, because in general such a substituent has a small rotation due to the near cancellation of large positive and negative components in the overlap integral. Small errors in location can therefore lead to large changes (percentagewise) in the value of this integral.

Transfer Reactions Involving Boron. VI. Physical Characterization and Chemical Properties of Aryl- and Alkylthioboranes^{1,2}

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received October 13, 1965

Abstract: The reaction of thiophenol with borane in tetrahydrofuran produces monomeric phenylthioborane. The structure of phenylthioborane was deduced from infrared and boron-11 magnetic resonance spectral data and molecular weight measurements. In contrast, benzyl mercaptan reacts with borane in tetrahydrofuran to produce a polymeric benzylthioborane. Aryl- and alkylthioboranes have been found to be effective ether cleavage reagents. These reagents readily reduce acids, aldehydes, and ketones to alcohols but do not react with esters or reactive organic halides. Aryl- and alkylthioboranes are effective hydroborating agents producing a product isomer ratio from unsymmetrical olefins different from that produced in hydroboration utilizing borane in tetrahydrofuran.

The reaction of mercaptans with diborane, with or without solvent, gives rise to a number of different products depending on the experimental conditions. Addition of methyl mercaptan to diborane at -78° leads to the formation of a methyl mercaptan-borane adduct which loses hydrogen with the formation of a solid product which by analysis corresponds to $\text{CH}_3\text{-SBH}_2$.⁴ The solid polymeric material was insoluble in ether, benzene, or chloroform. Treatment of the polymeric material with amines gave amine-borane complexes of the structure $\text{CH}_3\text{SBH}_2\text{NR}_3$. On heating *in vacuo* several fractions were obtained which were polymers of CH_3SBH_2 of varying chain length.

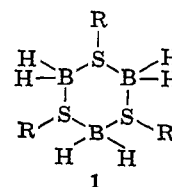
(1) Part V: D. J. Pasto and C. C. Cumbo, *J. Am. Chem. Soc.*, **86**, 4343 (1964).

(2) The authors gratefully acknowledge the financial support provided by the National Institutes of Health via Grant No. CA-07194 and a predoctoral fellowship to C. C. C.

(3) National Institutes of Health Predoctoral Fellow, 1963-1965. Taken in part from the Ph.D. thesis of C. C. C., University of Notre Dame, 1965.

(4) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

Similar results have been observed by Mikhailov and co-workers.⁵ The reaction of 2 moles of methyl mercaptan with diborane produced hydrogen and a gelatinous product which slowly became partially solid. This material was fractionated into a solid and a viscous liquid fraction. The solid fraction was converted to a trimer (1) on dissolution in tetrahydrofuran followed by distillation.



Treatment of ethyl or butyl mercaptans with diborane in diethyl ether gave polymeric alkylthioboranes

(5) B. M. Mikhailov, T. A. Shchegoleva, E. M. Shashkova, and V. D. Sheludyakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1218 (1962); *Chem. Abstr.*, **58**, 5499e (1963).