culations to be 29.2 kcal/mol higher in energy than the ground-state structure.[19,22] Thus, the distortion to the calculated unsymmetrical "pseudo η^3" coordination in the transition state stabilizes the structure by ~10 kcal/mol.

Comparison of our estimated transition state to those previously proposed for this and related systems reveals that our transition state is indeed novel. Our calculated Ti–C bond distances range from 2.15 to 3.40 Å for the interchanging ligands, compared to the metal–C distances ranging from 2.34 to 2.60 Å for the severely tilted η^5 ligands found in Cp_3MoNO. Because of the profound difference between the metal–C distances, the proposed transition state does not exhibit a tilted η^5 bonding configuration. In addition, optimization of the η^5Cp_3TiCl isomer generates a species with an energy 43.6 kcal/mol above the ground-state structure,[19] clearly arguing against the participation of such a conformation in the Cp exchange reaction. The interchanging Cp ligands are nearly planar, with the maximum twist angle between four adjacent carbons (i.e., C_1–C_2–C_3–C_4 and C_1–C_5–C_4–C_3) being ~6.5°. For comparison, the nonplanar η^3 coordination found in $Cp_2W(CO)_2$ is bent 20° out of plane.[3] The hydrogens remain in the plane of the Cp ring with the exception of the hydrogens on the σ carbons, which form a 119° angle with respect to the titanium.

Conclusion

In summary, the coordination of the interchanging ligands in the estimated transition state is significantly different from those proposed previously. Structurally, it resembles planar but unsymmetrical η^3 bonding. Electronically, the coordination is best described as stabilized η^1, with the stabilization due to delocalization of the Ti–C bond to adjacent π^* orbitals on the Cp's, and slight delocalization of the Cp π bonds into the metal valence shell.

Registry No. $CpTiCl_3$, 1270-98-0; Cp_2TiCl_2, 1271-19-8; Cp_4Ti, 63726-15-8.

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(22) Optimization of this structure omitted one mode to prevent the collapse of the η^1 geometry to an η^5 mode of bonding.

The Circular Dichroism of the Carbonyl n–π^* Transition: An Independent Systems/Perturbation Approach

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Abstract: An independent systems/perturbation approach is used to determine analytic expressions for the circular dichroism (CD) of the n–π^* transition in carbonyl compounds. It is shown that all available experimental data can be understood in terms of the predictions made by this theory. In general, for uncharged, nonpolar systems, the CD varies according to the octant sector rule of Moffitt et al.;[1] however, exceptions to this rule do arise for certain geometries and for situations in which the substituents on the compounds exclude the solvent in an unsymmetrical manner. Different geometry dependences are derived for polar and charged species and are found to explain the existing data.

1. Introduction

The circular dichroism (CD) of n–π^* transitions in carbonyl compounds has been the subject of speculation and analysis for many years. The octant rule of Moffit et al.[1] has proved to be a unifying feature for much of this work by providing a reference against which experiment has been compared. In its original form Moffit's octant rule (which we shall call the dynamic coupling octant (dco) rule for reasons that will become apparent) stated that the CD of the n–π^* carbonyl transition reflects positions of other parts of the molecule relative to the carbonyl group, according to the product $-xyz$, where (x, y, z) is a position vector in the right-handed coordinate system defined with the z axis along the C=O bond, the y axis in the carbonyl plane, and the origin centered on the nodal surface of the orbitals involved in the n–π^* transition (cf. Figure 1). The xz and yz reflection planes are thus defined by the approximate C_{2v} symmetry of the carbonyl part of the system, and the third plane by the orbitals involved in the transition. A perturbation theory analysis of the CD induced into the n–π^* transition of an achiral carbonyl chromophore by a chiral environment enabled Höhn and Weigang[2] to give a theoretical justification of the dco rule. This was the first use of what we shall call the independent systems/perturbation (ISP) approach (see, e.g., ref 3 and 4 for further details). An alternative formalism, which is somewhat less suited to the symmetry analysis approach of ref 7, is provided by the work of Buckingham and Stiles.[5]

Although the dco rule has proved to be highly successful, there are sufficiently numerous exceptions (e.g., ref 6–8) for closer examination to have been warranted. A number of empirical modifications to the dco rule have been made in attempts to extend its range of applicability. These have included the postulate that the third plane should be a curved surface, either convex[6] or concave[7] with respect to the carbonyl, or that it is the length of the primary zigzag[9] (see below) that determines the CD, or simply an anti-dco rule for some situations. Such empirical rationalizations, while they may be helpful for a given series of compounds, do not provide a global approach to carbonyl CD. Consideration of all terms in the ISP expansion of the CD provides a means of extending the analysis of Höhn and Weigang[2] to all potentially significant mechanisms for systems where the n–π^* transition can be considered to be essentially localized in an achiral carbonyl chromophore (see below). There is now available in the literature a wide range of systematically collated experimental data. In addition, the methodology for the symmetry analysis of ISP mechanisms has been developed for magnetic dipole allowed (mda)

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(1) Moffit. W.; Woodward, R. B.; Moscowitz, A.; Klyne, W.; Djerassi, C. *J. Am. Chem. Soc.* **1961**, *83*, 4013.

(2) Höhn, E. G.; Weigang, O. E. *J. Chem. Phys.* **1968**, *48*, 1127.

(3) (a) Schipper, P. E.; Rodger, A. *Chem. Phys.* **1986**, *109*, 173 and references therein. (b) Schipper, P. E.; Rodger, A. *Chem. Phys.* **1985**, *98*, 29.

(4) Richardson, F. S. *Chem. Rev.* **1979**, *79*, 18 and references therein.

(5) Buckingham, A. D.; Stiles, P. J. *Acc. Chem. Res.* **1974**, *7*, 258.

(6) Coulombeau, C.; Rassat, A. *Bull. Soc. Chim. Fr.* **1971**, *2*, 516.

(7) Bouman, T. D.; Lightner, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3145.

(8) Lightner, D. A.; Crist, B. V.; Kalyanam, N.; May, L. M.; Jackman, D. E. *J. Org. Chem.* **1985**, *50*, 3867.

(9) Kirk, D. N.; Klyne, W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1076.

0002-7863/88/1510-2361$01.50/0

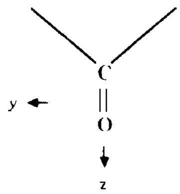

Figure 1. Coordinate system used for carbonyl systems with C_{2v} carbonyl chromophore.

transitions (n–π* is mda) during a study of mda d–d transitions in metal complexes.[3] Thus the time is right to proceed. As was the case for the d–d transitions, symmetry and chemical considerations enable the potentially important mechanisms for the n–π* CD to be identified. The remaining uncertainties about carbonyl n–π* CD can in this way be either resolved or seen in a framework that suggests direction for future work. As one might expect from the previous success of the dco rule, the isotropic dynamic coupling mechanism that gives rise to this rule is most often dominant. Once the conditions for its dominance have been established, we shall focus on those situations where simple dco rule behavior is not observed and see how the theory predicts precisely the observed behavior. The emphasis placed on the exceptions in this work should not be allowed to detract from the widespread success of the dco rule. Rather, the analysis of those situations where it is not operative should enable it to be applied with greater confidence than has been possible to date.

The next section presents the required theory in the form of an outline of the ISP approach to CD, giving the relevant expressions together with a discussion of their applicability. The relationship between the theory of section 2 and experimental (and calculated) data to be found in the literature forms the content of section 3. Since the theoretical analysis suggests that different behavior is operative for nonpolar, polar, and charged groups, this section is subdivided accordingly. The dco rule, as we shall see, proves to be applicable to uncharged nonpolar systems unless the net perturbing part of the system lies on or near one of the octant planes. Other mechanisms become significant in charged and polar systems.

2. Perturbation Approach to Circular Dichroism

The CD of a transition is given by the Rosenfeld equation

$$R = \mathrm{Im}\ \langle 0|\mu|1\rangle\langle 1|\mathbf{m}|0\rangle \qquad (1)$$

where R is the CD strength, Im denotes imaginary part, $|0\rangle$ is the initial state and $|1\rangle$ the final state of the transition, and μ and $\mathbf{m}$ are respectively the electric and magnetic dipole moment operators. The evaluation of the Rosenfeld equation requires the wave functions $|0\rangle$ and $|1\rangle$ to be known at least approximately. In some systems there is no alternative to directly determining $|0\rangle$ and $|1\rangle$ for the whole system. However, in many systems, the transition of interest is essentially localized in a nonexchanging subunit of the system (a chromophore). If this chromophore is (approximately) achiral, then the normal absorption spectrum can be approximated by considering the chromophore in isolation, and the CD can be described by the chiral perturbing effect of the rest of the system on the transition of interest. If such a chromophoric (or independent systems/perturbation) approach is applicable, then it makes the evaluation of the Rosenfeld equation much simpler: only wave functions of the smaller units need be determined and sometimes parametrization from normal absorption is possible. In addition, within a series of compounds, such as the carbonyl compounds of this work, it is possible to treat those parts of the CD expressions that depend on the same chromophoric units as transferable parameters. Not only does this save work, but it also enables trends to be followed more easily, making it apparent what effect a change in molecular structure will have.

The n–π* CD of carbonyl systems can be treated by using the ISP approach, since this transition is essentially localized on the carbonyl group and its neighboring atoms. This chromophore is usually achiral to a good approximation: C_{2v} symmetry for ketones and C_s symmetry for aldehydes (we shall return to the specific choice of symmetry group later). The remainder of the system then provides the chiral perturbation. This is the approach adopted by such workers as Höhn and Weigang[2] and Schellman[10] and is what led to the theoretical justification of the dco rule.[2] As we shall show, the ISP approach actually enables a general analysis of carbonyl CD, elucidating the general trends and making predictions that are in accord with experiment. By way of contrast, the calculations to be found in the literature have proceeded by determining approximate wave functions for the whole system. Recently, some progress has been made in relating the ISP approach to direct calculations of the Rosenfeld equation by expressing the operators within the Rosenfeld equation as sums analogous to those appearing in the perturbation expressions.[11]

2.1. Formalism. The details of the ISP approach, which are somewhat tedious and notationally complex, can be found elsewhere.[3] The carbonyl n–π* transition is magnetic dipole allowed, so we are interested in those mechanisms resulting from the ISP approach that depend on the magnetic dipole transition moment of this transition. The ISP approach and its application to d–d magnetic dipole allowed transitions are given in sufficient detail in ref 3 for only a brief outline of the approach to be required here. The actual expressions relevant for the carbonyl n–π* transitions differ somewhat from those for the d–d transitions, since mechanisms that could be disregarded for the metal complexes are, as we shall see, significant here.

The basis of the ISP approach is the partitioning of a chiral molecule into two essentially nonexchanging systems, one of which is achiral and contains the transition of interest and the other which provides the chiral perturbation and may itself be a composite system. (The practical implementation of this partitioning is discussed at the end of section 2.3.) The interaction between the two systems is taken to be purely electrostatic and so can be expanded in a multipole expansion. The wave functions of the whole system can then be expressed, using perturbation theory, in terms of the wave functions, transition moments, transition energies, and relative geometries of the component parts. The wave functions are then substituted into the Rosenfeld equation, resulting in a perturbation expansion with an infinite number of terms. If the ISP approach is to be of any practical use, the expressions must converge and do so relatively rapidly. This in fact proves to be the case (see, e.g., ref 3) unless A and C are very close and the molecular wave functions must be treated in their entirety. Each term in the ISP expansion contains a factor r^{-n}, where r is the distance between the origin of the achiral chromophore and the origin of a chromophore in the rest of the system; n increases with increasing order of perturbation theory and increasing order of the multipoles involved in the expression. Since r is typically greater than van der Waals radii, it is larger than the radius of convergence and only the lower order terms need be considered. The dominant term is then the one with smallest n whose moment products do not vanish by symmetry[3b] and which does not have very small moment products or geometry factors. The expressions quoted below satisfy these criteria. At this stage it should be noted that we are considering only those systems where the carbonyl has a preferential orientation with respect to its perturbers. The situation for rotationally averaged systems has been considered elsewhere.[12]

If we denote the achiral chromophore (the carbonyl, usually a ketone) by K and the set of chiral chromophores by {C}, then the CD of a magnetic dipole allowed transition is as follows:

$$R(\epsilon_k) = R^{\circ} + R'(\mathrm{KK}) + R'(\mathrm{KC}) + \text{higher order terms} \qquad (2)$$

where

$$R^{\circ} = \mathrm{Im}\ \mu^{0k}\cdot\mathbf{m}^{k0} = 0 \quad \text{since K is achiral}$$

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(10) Schellman, J. A. *Acc. Chem. Res.* **1968**, *1*, 144.

(11) Lightner, D. A.; Bouman, T. D.; Wijekoon, W. M. D.; Hansen, A. E. *J. Am. Chem. Soc.* **1986**, *108*. 4484.

(12) Schipper, P. E.; O'Brien, J. M.; Ridley, D. D. *J. Phys. Chem.* **1985**, *89*. 5805.

$$R'(\mathrm{KK}) = -\mathrm{Im}\sum_{\mathrm{C}}\sum_{k\neq j}\mathbf{m}^{k0}\cdot\{\mu^{0j}\langle j0|V|k0\rangle/(\epsilon_j - \epsilon_k) + \mu^{kj}\langle j0|V|00\rangle/\epsilon_j\} = \mathrm{Im}\sum_{C}\sum_{k\neq j}\mathbf{m}^{k0}\cdot\{[\mu^{0j}/(\epsilon_j - \epsilon_k)][r_\mathrm{c}^{-2}\mu_\alpha^{jk}\alpha C^0 + r_\mathrm{c}^{-3}\mu_\alpha^{jk}C_\beta^{00}(-\delta_{\alpha\beta} + 3\alpha\beta) + \tfrac{1}{4}r_\mathrm{c}^{-3}Q_{\alpha\beta}^{jk}(-\delta_{\alpha\beta} + 3\alpha\beta)C^0 + \tfrac{1}{2}r_\mathrm{c}^{-4}Q_{\alpha\beta}^{jk}(\delta_{\alpha\beta}\gamma + \delta_{\alpha\gamma}\beta + \delta_{\beta\gamma}\alpha - 5\alpha\beta\gamma)C_\gamma^{00}] + \mu^{kj}/\epsilon_j[r_\mathrm{c}^{-2}\mu_\alpha^{j0}\alpha C^0 + r_\mathrm{c}^{-3}\mu_\alpha^{j0}C_\beta^{00}(-\delta_{\alpha\beta} + 3\alpha\beta) + \tfrac{1}{4}r_\mathrm{c}^{-3}Q_{\alpha\beta}^{j0}(-\delta_{\alpha\beta} + 3\alpha\beta)C^0 + \tfrac{1}{2}r_\mathrm{c}^{-4}Q_{\alpha\beta}^{j0}(\delta_{\alpha\beta}\gamma + \delta_{\alpha\gamma}\beta + \delta_{\beta\gamma}\alpha - 5\alpha\beta\gamma)C_\gamma^{00}]$$

$$R'(\mathrm{KC}) = -\mathrm{Im}\sum_{\mathrm{C}}\sum_{b}\mathbf{m}^{k0}\cdot\{\mathbf{C}^{0b}\langle 0b|V|k0\rangle/(\epsilon_b - \epsilon_k) + \mathbf{C}^{b0}\langle kb|V|00\rangle/(\epsilon_b + \epsilon_k)\} = -\mathrm{Im}\sum_{\mathrm{C}}\sum_{b}\mathbf{m}^{k0}\cdot\mathbf{C}^{0b}[4\epsilon_b/(\epsilon_b^2 - \epsilon_k^2)][r_\mathrm{c}^{-3}\mu_\alpha^{0k}C_\beta^{b0}(-\delta_{\alpha\beta} + 3\alpha\beta) + 9r_\mathrm{c}^{-4}Q_{\alpha\beta}^{0k}C_\gamma^{c0}(\delta_{\alpha\beta}\gamma + \delta_{\alpha\gamma}\beta + \delta_{\beta\gamma}\alpha - 5\alpha\beta\gamma)]$$

where the $|0\rangle$ to $|k\rangle$ transition is, in the present work, the n–π* carbonyl transition, $\mu^{jl} = \langle j|\mu|l\rangle$ denotes an electric dipole transition moment between states $|j\rangle$ and $|l\rangle$ on K, similarly $\mathbf{Q}^{jl} = \langle j|\mathbf{Q}|l\rangle$ denotes the quadrupole transition moment and $\mathbf{m}^{jl} = \langle j|\mathbf{m}|l\rangle$ denotes the magnetic dipole transition moment on K, the carbonyl. $|j\rangle$ and $|l\rangle$ have transition energies from the ground state $|0\rangle$ of ϵ_j and ϵ_l, respectively. Similar notation is used for the ground state $|0\rangle$ and excited states $|b\rangle$ of C. C^0 is the charge of C, $\mathbf{C}^{00} = \langle 0|\mu_\mathrm{C}|0\rangle$ is the permanent electric dipole moment of C, $\mathbf{C}^{0b} = \langle 0|\mu_\mathrm{C}|b\rangle$ is the electric dipole transition moment on C between $|0\rangle$ and $|b\rangle$, r_c is the distance between the C origin and that of K (the subscript is often dropped for convenience), and $(x, y, z)_\mathrm{C} = (x, y, z)$ is the unit vector along the line from the origin of K to that of C in the coordinate system as defined by Figure 1. α, β, and γ stand for the Cartesian components $\{x, y, z\}$, $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$ and 0 otherwise, and summation over α, β, and γ is implied. It has been assumed in writing eq 2 that the effect of quadrupole and higher moments on C is negligible.

R'(KK) is known as the static coupling (sc) model since the radiation field couples the transition moments of K to static moments of {C}. Similarly, R'(KC) is known as the dynamic coupling (dc) model as it involves coupling of transition moments on both K and {C}. Application of the generalized selection rules according to the methods used in ref 3 results in the symmetry-adapted expressions for the carbonyls given in eq 3 and 4. The terms included in these equations are those whose carbonyl-dependent moment products are totally symmetric in the point group of the carbonyl chromophore. Note that the CD expressions retain explicit dependence on the position of the chiral perturbers in the carbonyl coordinate system; hence, if one mechanism, or term in the expansion, is dominant, then a traditional sector rule results, otherwise a more complicated geometry dependence is to be expected.

$$C_s\text{:}\quad R_{\text{n}-\pi^*} = \mathrm{Im}\sum_{\mathrm{C}}S_1 + S_2 + S_3 + \ldots \tag{3}$$

where

$$S_1 = r_\mathrm{c}^{-2}\sum_{k\neq j}\sum_{\chi}\{m_z^{k0}\mu_z\mu_x/(\epsilon_j - \chi\epsilon_k)\}C^0\chi \tag{3a}$$

$$S_2 = r_\mathrm{c}^{-3}\sum_{k\neq j}\sum_{\chi}\{m_z^{k0}\mu_z\mu_x/(\epsilon_j - \chi\epsilon_k)\}[C_x^{00}(3x^2 - 1) + C_y^{00}(3xy) + C_z^{00}(3xz)] + \{m_z^{k0}\mu_zQ_{xy}/(\epsilon_j - \chi\epsilon_k)\}(\tfrac{3}{2}C^0xy) + \tfrac{3}{2}C^0xz] + \tag{3b}$$

$$S_3 = r_\mathrm{c}^{-3}\sum_{b}[4\epsilon_b/(\epsilon_b^2 - \epsilon_k^2)]m_z^{k0}\mu_x^{0k}[3C_z^{0b}C_z^{b0}xz + C_z^{0b}C_x^{b0}(3x^2 - 1) + 3C_z^{0b}C_y^{b0}xy] \tag{3c}$$

$$C_{2v}\text{:}\quad R_{\text{n}-\pi^*} = \mathrm{Im}\sum_{\mathrm{C}}T_1 + T_2 + T_3 + \ldots \tag{4}$$

where

$$T_1 = r_\mathrm{c}^{-3}\sum_{k\neq j}\sum_{\chi}\tfrac{3}{2}[m_z^{k0}\mu_zQ_{xy}/(\epsilon_j - \chi\epsilon_k)][C^0xy] = r_\mathrm{c}^{-3}K_{\mathrm{mom}}^{\mathrm{ch}}[C^0xy] \tag{4a}$$

$$T_2 = r_\mathrm{c}^{-4}\sum_{k\neq j}\sum_{\chi}2[m_z^{k0}\mu_zQ_{xy}/(\epsilon_j - \chi\epsilon_k)] \times [C_x^{00}y(1 - 5x^2) + C_y^{00}x(1 - 5y^2) - 5C_z^{00}xyz] = r_\mathrm{c}^{-4}K_{\mathrm{mom}}^{\mathrm{dip}}[C_x^{00}y(1 - 5x^2) + C_y^{00}x(1 - 5y^2) - 5C_z^{00}xyz] \tag{4b}$$

$$T_3 = r_\mathrm{c}^{-4}\sum_{b}12[m_z^{k0}Q_{xy}^{0k}\epsilon_b/(\epsilon_b^2 - \epsilon_k^2)] \times [5C_z^{0b}C_z^{b0}xyz + C_z^{0b}C_x^{b0}y(5x^2 - 1) + C_z^{0b}C_y^{b0}x(5y^2 - 1)] = r_\mathrm{c}^{-4}\sum_{b}12K_{\mathrm{mom}}^{\mathrm{pol}}[5C_z^{0b}C_z^{b0}xyz] + \tag{4c}$$

$$r_\mathrm{c}^{-4}\sum_{b}12K_{\mathrm{mom}}^{\mathrm{pol}}C_z^{0b}C_x^{b0}y(5x^2 - 1) + C_z^{0b}C_y^{b0}x(5y^2 - 1)] \tag{4d}$$

where $\chi = 1$ or 0. If $\chi = 1$ then the K-state labels $0j,jk$ are inserted on $\mu_z\mu_x$ or μ_zQ_{xy}. If $\chi = 0$ then the K-state labels $kl,l0$ are inserted. The coordinate system used for the C_{2v} expressions is that illustrated in Figure 1. That for C_s is similar, the z axis being defined to be the direction of polarization of the n–π* transition, so the coordinate system will be rotated slightly.

2.2. Discussion. Consideration of molecular models indicates that those ketone systems for which there are experimental data in the literature have approximate C_{2v} symmetry. We shall therefore consider the CD behavior predicted by eq 4.

To establish the dominant source of CD in a given situation, we first consider the term with the lowest inverse r dependence. If this term does not vanish because of either symmetry constraints or physical properties of the system, such as geometry or absence of charge, then it should provide the majority of the CD intensity. Thus for C_{2v} chromophores, we would first consider the r^{-3} term in eq 4a to see if it might be dominant. The magnitude of (4a) depends on the existence of a charged species in the molecule, its distance from the carbonyl, and its orientation with respect to the xz and yz planes. Thus (4a) will be dominant if there is a charged species that does not lie close to the xz or yz planes (and is located relatively near the carbonyl group). Under such circumstances eq 4a tells us that the CD varies with the position of the perturber according to a simple quadrant, i.e., xy, dependence. The sign of the CD is dependent on the sign of xy, the sign of $K_{\mathrm{mom}}^{\mathrm{ch}}$, and the sign of the charge. The small amount of experimental data that is currently available suggests that $K_{\mathrm{mom}}^{\mathrm{ch}}$ is probably negative (see section 3.3), so for a positively charged inducer located behind the carbonyl (the usual situation) with $z < 0$, we would expect to see a CD of opposite sign from the dco prediction (but would expect one of the same sign as the dco prediction for $z > 0$). The converse is appropriate for negatively charged inducers. In addition to the different geometry dependence, the variation of the intensity of (4a)-dominated transitions is different from dco-dominated transitions since, (4a) is independent of polarizability, and the K moment products differ for the two situations.

Historically, the charge-dependent mechanism of eq 4a is of great interest, since it was the first mechanism that seemed appropriate for carbonyl n–π* CD. Schellman[13] analyzed this mechanism (which is the one-electron or the static coupling model of Condon et al.[14] with the chiral perturbing field being due to a collection of charges) using symmetry. Thus he derived the geometry dependence of eq 4a for C_{2v} systems. Much use has been made of Schellman's symmetry analysis because of its appealing simplicity and the way it reflects the symmetry of the system. However, his results are often applied to systems for which they are not applicable. *The dominant mechanism for any given situation must be established before the results of a symmetry analysis can be applied.* This is clearly illustrated in the context of metal complexes where Schellman's results have been used widely, but extensive studies by Richardson et al.[4] have shown that this mechanism is not significant in metal complexes. In carbonyls, however, the static couplic model is significant for charged systems, where the charged chromophore is near the carbonyl.

If (4a) is not dominant, then the next terms to be considered are the r^{-4} terms. These are of two types: (i) static coupling terms

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(13) Schellman, J. A. *J. Chem. Phys.* **1966**, *44*, 55.

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

dependent on the components of the permanent dipoles of $\{C\}$, and (ii) dynamic coupling terms dependent on the polarizabilities of $\{C\}$ ($C_z^{0b}C_\alpha^{b0}$ together with the energy factor is the $z\alpha$ component of the polarizability of C). Systems whose $\{C\}$ are nonpolar reduce to consideration of only the polarizability terms, whereas systems with polar $\{C\}$ have a complex superposition of the two types. The relative sizes of the three dipolar terms in (4b) depend on the orientation of the chromophores in space and the directions of the dipoles. $K_{\mathrm{mom}}{}^{\mathrm{dip}}$ appears to be positive (see section 3.2), so examination of the structure of a molecule can lead to predictions of the sign of the dipolar CD contribution. If one of the dipolar terms clearly dominates the others, then its geometry term gives a simple dependence of the CD on the geometry of the system, i.e., a sector rule.

The polarizability contribution to the CD is always present. It will generally not be dominant in a charged system, may be dominant in a polar system, and will be dominant in an uncharged, nonpolar system. There are three polarizability terms in (4c) and (4d), which have the same geometry dependence as the corresponding dipolar terms in (4b); however, the polarizability terms have one very significant difference from the dipolar ones, namely that the zz term of eq 4c will generally be dominant. The reason for this is that it depends on the isotropic polarizability whereas the terms in (4d) depend only on the smaller anisotropic polarizability. Thus the polarizability contribution to the CD will have an xyz (i.e., octant) geometry dependence unless $xyz \approx 0$. From comparison with experiment, $K_{\mathrm{mom}}{}^{\mathrm{pol}}$ can be seen to be negative, and $C_z^{0b}C_z^{b0}$ is positive, so the isotropic dynamic coupling CD of (4c) will have sign $-xyz$ in accord with the dco rule. For alkyl and amine systems eq 4c can be expected to describe the CD. Support for this conclusion can be readily found in the literature. For example, ref 17, illustrates how the dco rule can be used to understand the temperature variation of CD in oxoquinolizidines in terms of a number of conformers. See also ref 1, 2, 6–9, 11, and 15–19.

The anisotropic polarizability terms of eq 4d may become significant if $xyz \approx 0$ for the inducing chromophores, and the system is noncharged and nonpolar. The first point to note is that the CD of such a system would be smaller than a similar one with net perturbers in different positions. The geometry dependences of the two anisotropic dc terms are respectively $y(5x^2 - 1)$ and $x(5y^2 - 1)$. Since $K_{\mathrm{mom}}{}^{\mathrm{pol}} < 0$, the sign of the CD follows from the sign of the geometry factors and of the anisotropic polarizabilities. At this stage it is appropriate to note that higher order terms do not need to be considered when $xyz \approx 0$, since higher order isotropic terms also depend on xyz.

C_s carbonyl symmetry and hence eq 3 are of less immediate use due to lack of experimental data. C_s symmetry is clearly appropriate for aldehydes and also for strongly distorted ketone systems. From eq 3 it is apparent that the distortion of an uncharged nonpolar ketone must provide a significant out-of-plane electric component to the $n-\pi^*$ transition moment for eq 3 not to be dominated by the terms in eq 4 (which are higher order terms for the C_s system). For charged and polar systems the C_s symmetry is important if the moment product $m_z\mu_z$ has a component symmetric with respect to the xz reflection plane. Equation 3 is applied in the same way as eq 4, except that for aldehydes it is necessary to rotationally average the expression about the first C–C bond due to the nonrigidity of such a system.

2.3. Chromophores. In our discussion so far we have talked about the chromophoric units $\{C\}$ without ever really defining them. Having seen how they are used, we are now in a position to define them a little more precisely. It is not always easy to divide the noncarbonyl part of the system into nonexchanging units; however, that problem can be circumvented by noting that we only used the charge, permanent dipole, and polarizability of $\{C\}$. The locality of charges and dipoles can be readily determined for the accuracy required in a qualitative analysis, and polarizabilities can be approximately expressed as sums of bond polarizabilities or polarizabilities of groups such as CH_2 units.[19] (This is probably the result of the localized nature of the lowest lying transitions in saturated carbonyls, which the energy denominators in eq 2–4 cause to be the dominant contributors to the polarizability.) Thus $\{C\}$ is represented by a set of localized charges, dipoles, and polarizabilities.

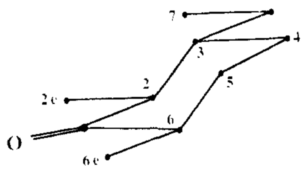

Figure 2. Structure of decalones.

Isotropic polarizabilities are readily available (see, for example, ref 20). For the practical application of eq 4c, we note that the geometry dependence causes units of equal polarizabilities on either side of a reflection plane to have no net effect on the CD. As the polarizability of $-CH_3$ is only slightly larger than that of $>CH_2$ (molar bond refraction of C–H = 1.68 cm^3 and of C–C = 1.30 cm^3 [20]), the common practice of cancelling contributions from C's symmetric about a carbonyl symmetry plane in order to determine the dco CD is approximately valid. (It should, however, be noted that Lightner et al.[11] found that it was dangerous to assume complete cancellation.) We shall denote the "noncanceling" contributors to the CD as *net perturbers*. At this stage we should note that the isotropic polarizability of amine groups is a little less than that of alkyl groups, e.g., the molar refraction of NH_3 is 5.67 cm^3 and that of CH_4 is 6.58 cm^3,[20] and thus one cannot expect complete cancellation of opposite C and N perturbations.

There are a number of approximations inherent in these definitions of the $\{C\}$; for example, by proceeding in this manner we are ignoring any differences in environments of C atoms and C–C bonds. Such considerations must be accounted for in a quantitative study; however, they are a perturbation on the perturbation that induces the CD and can usually be ignored for a qualitative or semiquantitative study.

3. Applications

The discussion of the previous section indicated the general trends in behavior that we might expect for charged systems, polar systems, and uncharged nonpolar systems. For charged systems we would expect a quadrant sector rule to be operative and hence observe non-dco behavior. For polar systems there are potentially a number of significant mechanisms and there is the possibility of dco behavior. For uncharged nonpolar systems, unless all perturbing groups lie on or near a reflection plane, we would expect dco behavior to be operative. There is to be found in the literature a wide variety of data supporting the applicability of the dco rule for these systems; however, some apparent exceptions have been recorded. We shall show that the assumptions inherent in the application of the dco rule to such situations, together with the theoretical predictions from eq 4, will prove sufficient for the CD of these systems to be understood. In the remainder of this section we shall specifically look at two types of systems: (i) molecules for which eq 4 suggests behavior other than dco, and (ii) molecules that apparently do not exhibit dco behavior, but that eq 4 suggests should do so. We shall begin our discussion with the uncharged nonpolar systems, as the conclusions made in the study of these compounds are needed for the other systems.

3.1. Uncharged Nonpolar Systems. 3.1.1. Deuterium. Deuterium-substituted compounds, which have often been seen as being slightly anti dco, are a useful illustration of the relative contributions of substituents with different polarizabilities to the CD.

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(15) Lightner, D. A.; Jackman, D. E. *J. Chem. Soc., Chem. Commun.* **1974**, 344.

(16) Lightner, D. A.; Chang, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 3015.

(17) Mason, S. F.; Schofield, K.; Wells, R. J. *J. Chem. Soc. C* **1967**, 626.

(18) Johnson, R. A.; Murray, H. C.; Reineke, L. M.; Fonken, G. S. *J. Org. Chem.* **1968**, *33*, 3207.

(19) (a) Snatzke, G.; Eckhard, G. *Tetrahedron* **1968**, *24*, 4543. (b) Snatzke, G.; Ehrig, B.; Klein, H. *Tetrahedron* **1969**, *25*, 5601.

(20) Vogel, A. *A Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, New York, 1978.

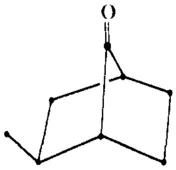

Figure 3. Structure of (1*R*)-*exo*-2-methyl[2.2.1]bicycloheptan-7-one.

As Lightner et al.[23] noted, the D–C bond length is smaller than the H–C bond length so its polarizability is smaller. H–C therefore makes a larger contribution to the CD than does its opposite D–C contribution, and the CD is dco, but dominated by the "opposite" H rather than the D (thus appearing to be anti dco if only the D is considered).

3.1.2. Decalones. The 2-equatorially substituted decalone compounds (see Figure 2) are compounds in which $x = 0$ (and z is also small), so the isotropic dc mechanism of eq 4c would be predicted to make a small contribution to the CD. The observed CD is predicted to be small and largely due to the C_zC_x anisotropic dc mechanisms of eq 4d. Since $y > 0$, the sign of the CD is determined by the sign of the zx component of the anisotropic polarizability. This is negative if the most significant transitions are assumed to lie along the C–C bond, suggesting a negative CD contribution from a 2-equatorial substituent, as is in fact observed. In addition, the magnitude of the 2-equatorial CD compared with that of the 3-axial and 3-equatorial (where dco behavior is expected) supports the earlier statement that the anisotropic mechanisms are generally insignificant compared with the isotropic ones.

By considering the difference in optical rotatory dispersion (ORD) between the compound with 7 = H and 7 = CH_3 in Figure 3, Coulombeau and Rassat[6] deduced that position 7 gave rise to a negative ORD (and hence CD). This is not consistent with the dco prediction for the decalone conformation of Figure 3, and it led them to propose a curved third surface (with opposite curvature from that of Bouman and Lightner[7]). Consideration of the molecules in question suggests an alternative reason for the negative ORD. In addition to the conformer of Figure 3, there is another conformer that would have a negative dco CD. Although statistically less probable, the alternative conformer could dominate the CD since it has two net perturbers rather than the one of the Figure 3 structure, and the r_c's of the inverted conformer are about $^4/_5$ those of the Figure 3 structure. The same line of reasoning applies to most other compounds of ref 3, which appeared to be contravening the dco rule. The remaining compounds that are suggested to have non-dco CD have used reference compounds to reach this conclusion that are so different as to make the comparison invalid.

3.1.3. "Primary Zigzag Rule". The empirical observation of Kirk and Klyne,[9] that the length of the "primary zigzag" (i.e., the zigzag of C–C bonds coplanar with the C=O bond) in hydrocarbon compounds is directly related to CD, appears at first sight to be unrelated to a mechanistic approach and hence to bear no relationship to a sector rule such as the dco rule. However, further investigation of the types of compounds they examined results in a relationship being established between the two approaches. It is apparent from molecular models that Kirk and Klyne's long primary zigzag compounds that exhibit enhanced positive (which is the sign predicted by the dco rule) CD's compared with their parent bicyclic ketones are presicely those whose structures enable some of the additional CH_2's to come comparatively close to the carbonyl chromophore in such a way as to make a large positive dco contribution. Structures without extended primary zigzags do not have sufficiently flexible structures for this to be the case. Thus the work of Kirk and Klyne can in general be seen to be corroborating the applicability of the dco rule for hydrocarbon systems.

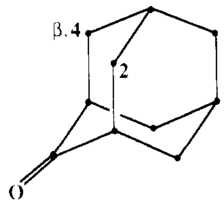

Figure 4. Structure of adamantones and labeling positions as used in this work. β-Equatorial substituents are directed into the page, and β-axial substituents are approximately in the plane of the page directed toward the carbonyl group.

3.1.4. Amines. As noted above the CD of N-containing saturated structures would be expected to be dominated by dco behavior. Analysis of such systems is more complex than that of purely alkyl ketones due to the slight difference between C and N polarizabilities. Since amine groups have a lower polarizability than the corresponding alkyl groups (see above), the effect is similar to that of deuterium and hydrogen in section 3.1.1. Reported exceptions (e.g., ref 24) to dco behavior have resulted from only considering the N contributions to the CD whereas both C's and N's must be considered to deduce the net CD.

3.1.5. β-Axial-Substituted Systems. The CD of β-axial-substituted alkyl ketones (we shall consider the 2-position β substituent throughout this section; cf. Figure 4) should, according to the discussion of section 2, follow dco behavior. However, there are some calculations (which are not conclusive) and also experimental data that suggest that the CD for such systems does not follow the dco rule and is most likely to be of opposite sign from its predictions. We shall begin by discussing the evidence for this, and then see that it is precisely what might have been expected had solvent effects not been ignored in the application of the dco rule.

The first suggestion that β-axial-substituted alkyl ketones might not follow the dco rule was the calculation of Pao and Santry[21] on the CD of a compound with $-CH_3$ substituted for the β-axial proton of cyclohexanone (see Figure 4 for labeling of cyclohexanone by considering only the labeled part of the adamantone structure). However, as they themselves note, their calculation is not conclusive due to the size of the system. Later experimental work of Snatzke et al.[19] on the rigid β-axial methyladamantone (see Figure 2) seemed to support their theoretical prediction. *exo*-2-Methylbicyclo[2.2.1]heptan-7-one[22] (Figure 3) and steroidal α-ketones[9] also exhibit this behavior. It is appropriate at this stage to make mention of other calculations to be found in the literature. The calculations of Bouman and Lightner[7] on simple ketones (methyl ethyl ketone, ethyl propyl ketone, and propyl butyl ketone), in fixed geometries so that all C's except the terminal methyl, C_T, are symmetric about the xz plane (C_T was therefore assumed to be the only net perturber), in general support the validity of the dco rule. However, some anomalous "holes" appeared, and the results near the xy plane suggested to the authors that the third surface should be curved (convex about C=O, resulting in the β-axial position changing octants). These results cannot be completely understood in terms of the mechanisms of eq 3 and 4. Some of the suggested non-dco behavior is due to the substituents lying close to reflection planes of the C_{2v} chromophore so the mechanisms of eq 4d become significant, some of it may be due the unstable geometries forced on the systems, and the remainder may well be due to inaccuracies in the calculations. The problems with CD calculations for β-axial systems is supported by the better calculations of Bouman and Lightner[11] on 4-axially substituted adamantones. The CD calculated for the geometry suggested by a molecular mechanics calculation is in accord with a dco prediction; however, that for the similar idealized cyclohexanone geometry is in disagreement with the prediction. At this stage all that can be concluded is that care must be taken in interpreting the results of a calculation, and we shall restrict our attention to experimental data.

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[21] Pao, Y. H.; Santry, D. P. *J. Am. Chem. Soc.* **1966**, *88*, 4157.

[22] Lightner, D. A.; Jackman, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 1938.

[23] Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 1983.

[24] Hudec, J. *Chem. Commun.* **1970**, 829.

The rigid geometry of β-axial compounds is such that the dco mechanism of eq 4c is predicted to be dominant for the CD of an isolated molecule. Consideration of molecular models thus leads to the conclusion that a gas-phase CD spectrum of a β-axial compound (if one were available) should have a positive n–π^* CD if the substituent is a methyl or ethyl group and will become less positive, and finally negative, with increasing chain length since subsequent C's will project into negative dco octants a large percentage of the time. As the available experimental data for these compounds are in solution, we must now consider the modifying effect of the solvent on the observed CD. Up until this point we have implicitly assumed that the solvent had no appreciable affect on the CD.

Solvent effects will clearly be significant when the solvent reacts with the solute being studied; however, this situation is outside the scope of the present work, and we shall limit our consideration to nonreacting solvents. In addition, we shall not consider the effect of a chiral solvent as this has been dealt with elsewhere.[12] An achiral solvent molecule is part of the chiral environment of the molecule being studied, since the chiral molecule causes asymmetric solvent packing. Thus the solvent might be expected to have some effect on the CD. In general, this effect will be small compared with the total CD for the following reasons: (i) van der Waals radii are larger than bond lengths so that solvent molecules are usually further from the achiral chromophore and thus their contribution is smaller than the net perturbers of the carbonyls. (ii) Solvent molecules will generally be rotationally averaged with respect to the solute, so they will contribute only through those terms dependent on isotropic C moment products, i.e., through the isotropic polarizability part of eq 4c (assuming uncharged solvent). (iii) The contribution from a solvent molecule on one side of the solute will on average be approximately cancelled by the contribution from one on the opposite side. Solvent effects will become significant when the effect of these factors, and especially (iii), is reduced. A definitive analysis of these effects will clearly require knowledge of the solvent packing about the solute, and calculations to elucidate this are in progress; nonetheless it is possible to make a reasonable qualitative assessments of these effects.

One situation in which the net cancellation of solvent-induced CD does not occur is when the perturbing chromophore prevents free access by the solvent to any part of one octant but allows access to the corresponding part of a "reflected" octant. If this is the case, then there will be a net contribution to the CD from the solvent in the reflected octant, which will have the opposite sign from the dco contribution of the substituent. In some circumstances, the solvent contribution will be the dominant determiner of the observed CD. The intensity of the solvent contribution to the CD will depend upon the density of the solvent and upon the extent to which the solvent is excluded by the substituent (as well as the nature of the solvent). Clearly, for a given solvent, both of these factors will vary with temperature, implying that solvent effects will introduce a temperature dependence into the CD. This is significant since CD, being a spectroscopic phenomenon, is of itself largely temperature independent.

It appears that solvent effects must be considered with β-substituted compounds (see Figure 4). β-Equatorial substituents will restrict solvent access to only a small extent; thus dco CD is expected. In fact the CD of β-equatorial compounds can be understood almost completely in terms of only the dco contribution of that substituent: each additional C adds an amount to the total CD which depends on its distance from the carbonyl according to the r^{-4} dependence and the polarization of each carbon decreasing with decreasing number of H's attached to it. There is a small variation with temperature of the CD of β-equatorial substituents[11] which reflects the existence of a comparatively small solvent "hole" and so a small net negative solvent contribution to the CD. In contrast to the β-equatorial systems, the β-axial systems would be expected to exhibit a large solvent dependence since (i) the geometry of these systems restricts solvent access significantly and (ii) the solvent molecules whose CD contribution is not cancelled are in the $x > 0, y < 0, z < 0$ (negative dco) octant and are located close to the carbonyl. Thus this solvent "hole" will result in a net negative contribution to the CD arising from the solvent, which may dominate the positive contribution arising from the β-axial substituent. In this context it should be noted that solvent density increases with decreasing temperature, so that the asymmetric effect of a solvent hole will increase with decreasing temperature; other temperature effects will be related to the mobility of the solvent and solute. The available experimental data are consistent with the deductions that can be made from the hypothesis of restricted solvent access, or a solvent "hole"; however, further experimental data (ideally gas phase) as well as molecular mechanics determinations of the geometries of solute/solvent systems are required. We shall now examine what data are available.

For large enough solvent molecules the presence or absence of a β-axial substituent will not affect its ability to approach the carbonyl chromophore, implying that the CD should be determined by the dco contribution of the substituent. In accord with this, Snatzke et al.[19b] found that 2-*axial*-methyl-β-adamantone in bulky isooctane has positive CD. However, in the less bulky solvent dioxane/ethanol[19b] the CD is negative. Another situation where the CD could be expected to follow the dco prediction of the β-axial substituent is where both solvent and substituent are sufficiently small that solvent molecules can approach despite the presence of the substituent. The extreme case of this is for a deuterium substituent, where the behavior discussed in section 3.1.1 is predicted and observed.[11] In practice, most substituents (including CH_3) are of an intermediate size and thus allow partial access by the solvent to the carbonyl chromophore. As temperature increases, one would expect the solvent to penetrate further into this sterically hindered region, and thus the negative contribution should decrease with increasing T; this trend will be reinforced by the simultaneous decrease in solvent density. The expected temperature dependence is observed for β-axial $-CH_3$, $-CH_2CH_3$, and $-CH(CH_3)_2$, being most noticeable for the methyl group, where in methylcyclohexane/isopentane the CD is actually just positive, +0.08, at 25 °C (significant solvent effect clearly is operative even at 25 °C, since the axial substituent would have a larger dco CD than its equatorial counterpart, which is +1.5). The solvent dependence gradually decreases with increasing size of substituent, the limit of this being reached for the very bulky $-C(CH_3)_3$, where there is very little solvent effect in diethyl ether/isopentane/ethanol, and a small effect in methylcyclohexane/isopentane. (The direction of the change in CD with temperature in methylcyclohexane/isopentane in fact suggests that solvent approach is easier at lower temperatures where there is less motion of the substituent and more open conformations remain long enough for solvent molecules to approach.) It is difficult to say whether the trend observed in $-CH_2CH_2C(CH_3)_3$ is due to solvent effects or simply to increasing time spent in energetically favorable conformations that have negative dco CD. Due to the size of the substituent, the latter is probably the more significant factor.

3.1.6. Summary. A number of important points emerge from this discussion. Although the isotropic dc mechanism is generally dominant for alkyl and amine ketones, this does not automatically mean the simplest of dco behavior can be expected. If the net perturbers have $xyz \approx 0$, an anisotropic polarizability term will be dominant. Consideration must also be given to the contribution of energetically less likely conformations since they may dominate the CD spectrum and the relative contributions of groups such as H and D, and C and N must be correctly estimated. Finally, from the above discussion it would appear that the effect of the solvent cannot always be ignored. In most situations solvent molecules show little effect on the carbonyl chromophore CD; however, the β-axially substituted systems appear to create a "solvent hole" between the carbonyl and the substituent into which some solvent molecules may not penetrate. As a result the contribution to the CD of a solvent molecule on the "opposite" side of the molecule is not cancelled so it makes a net dco contribution to the CD of opposite sign from that of the β-axial substituent.

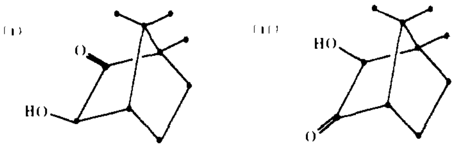

Figure 5. Structure of bornanones: (i) *exo*-bornan-2-one; (ii) *exo*-bornan-3-one.

This may result in a net CD of opposite sign from that suggested by the β-axial substituent.

3.2. Polar Chromophores. Systems containing chromophores with permanent dipoles potentially have the most complex CD from a mechanistic point of view, since both the dipolar mechanisms and the polarizability mechanisms are r^{-4} and thus competitive. As a result, in a series of compounds with halogen substituents we might expect the dipolar mechanism to be most significant for F and to decrease in importance down the periodic table as polarizabilities increase and dipole moments decrease. The signs of the CD resulting from the dipolar mechanisms depend on the direction of the permanent dipole as well as on the geometry factors. From eq 4b it is apparent that the geometry dependences of the components of the dipolar mechanisms are the same as that of the polarizability mechanisms. However, due to the different moments involved, the signs of the contributions and their relative weightings will be different. As C chromophores are not restrained in any way to align themselves with the carbonyl system axes, a dipolar CD is likely to be a superposition of three terms of comparable magnitude. This is in distinct contrast to the polarizability mechanisms where the C_zC_z term almost always dominates. We shall consider some experimental data to investigate this further.

3.2.1. β-Substituted Adamantones. Snatzke and Eckhard[19a] studied a range of β-substituted adamantones (cf. Figure 4). The 4-equatorial compounds follow precisely the behavior suggested above: Cl, Br, I, and also N_3, follow a simple dco rule with the magnitudes of their positive CD's reflecting their polarizabilities as required for the isotropic dc mechanism; F, on the other hand, has a small negative CD that bears no direct relationship to its polarizability. The dipole mechanisms therefore appear to be the most significant contributors for the 4-equatorial F-substituted compound. Given that this is so, consideration of the direction of the dipole and eq 4b geometry dependences should enable the sign of $K_{\mathrm{mom}}{}^{\mathrm{dip}}$ to be deduced. $K_{\mathrm{mom}}{}^{\mathrm{dip}}$, in a qualitative analysis, can then be taken as a transferable parameter. Consideration of a molecular model suggests that $C_x{}^{00} \approx 0$ and $C_y{}^{00} \approx -C_z{}^{00}$ and $x,y > 0$, $z < 0$, so the $C_y{}^{00}$ and $C_z{}^{00}$ terms both have the same sign. This is negative (as is required to counter the positive dco contribution) if the K moment product is positive. We therefore deduce that $K_{\mathrm{mom}}{}^{\mathrm{dip}} > 0$.

The 4-axial F CD can once again be understood in terms of the dipolar mechanism being dominant. Here, $C_x{}^{00}$ and $C_z{}^{00} > 0$, so (using a positive K moment product as deduced above) the predicted CD is positive, which is what is observed in a variety of solvents. The larger halogens and N_3 are more complex in that the C–X bond is large enough to form a hole from which solvent molecules can be excluded. Thus, although the dominant contribution of the halogen to the CD would be expected to be positive dco as in the equatorial case, the dco contribution from the solvent would be negative (cf. the purely hydrocarbon systems above), resulting in the observed negative CD.

3.2.2. Hydroxy- and Acetoxybornanones. Hydroxy- and acetoxybornanones (see Figure 5 for structures) are compounds for which the dipolar mechanisms may be significant. We have already seen that the dipolar mechanism was dominant for F, but could be ignored for Cl substituents, and on a simple electronegativity basis, one might expect O to fall somewhere between these two. Bartlett et al.[25] determined the contribution of the hydroxy and acetoxy groups to the CD by considering the difference in CD between unsubstituted and endo- and exo-substituted bornanones. Except for *endo*-2-hydroxybornan-3-one in methanol, which had a very small contribution of the same sign as the dco CD, they found that the sign of the additional CD was not in accord with a simple dco prediction. We shall first consider the predictions of the dipolar mechanisms for these systems and shall then consider the effect of the solvent. Once the directions of the dipoles and the geometry factors have been determined, the signs of the dipolar CD contributions can be predicted by using $K_{\mathrm{mom}}{}^{\mathrm{dip}} > 0$ and then compared with the observed CD. In all the compounds of interest the average dipole is largely x-directed, and so we need only consider the $C_x{}^{00}$ term.

For *exo*-2-hydroxybornan-3-one, the appropriate geometry factor, $y(1 - 5x^2)$, is positive and $C_x{}^{00} < 0$; we therefore predict a negative dipolar contribution to the CD. *exo*-3-Hydroxybornan-2-one, on the other hand, has a negative geometry factor, resulting in the prediction of a positive dipolar CD contribution. Both of these predictions are in accord with experiment. A similar line of reasoning applies to the *exo*-acetoxy compounds with the same result. For the endo compounds the geometry factors have opposite signs, resulting in a positive contribution for the *endo*-2-bornan-3-ones and a negaitve one for the *endo*-3-bornan-2-ones; again this is in accord with experiment. Thus in general the dipolar CD can be seen to be the major contributor to the CD of these compounds. For a quantitative account of their CD, it would also be necessary to include solvent exclusion effects; however, the similarity between the observed CD of the hydroxy and acetoxy groups, the endo and exo forms, and the bornan-2-ones and bornan-3-ones suggests that this will not change the qualitative predictions.

In methanol, a new type of solvent effect must be considered, as this system admits the possibility of hydrogen bonding. In particular, the methanol will strongly hydrogen bond to the hydroxyl and also the carbonyl, resulting in a preferential orientation of the hydroxyl group: almost parallel to the carbonyl. As a result, the contribution from the bridging methanol dipole is positive, that from the hydroxyl is negative, and there is therefore substantial cancellation of these dipolar contributions to the CD. In *endo*-2-hydroxybornan-3-one and *exo*-2-hydroxybornan-3-one, the presence of the nearby methyl groups will prevent the approach of further methanols to the carbonyl, and we thus expect the CD to be small; in both cases it is observed to be small and negative. In the bornan-2-ones, however, there are no such restrictions on the approach of further solvent molecules. These will be free to adopt other geometries about the carbonyl, with the result that the solvent contribution to the CD will substantially cancel. The CD is therefore dominated by the hydroxy dipole, although we note that the solvent will still give rise to a preferential orientation of the hydroxyl group.

3.2.3. Cholestanones. Other examples of anti-dco behavior have been reported by Bull and Enslin[26] in steroidal α-ketols and their acetates. These compounds provide perfect examples of situations where the dco rule is predicted to be invalid. In some the substituent lies in the yz plane, some have a solvent hole created by the substituent and carbonyl providing the potential for solvent exclusion, some have a variety of conformers, and all have the potential for both dipolar and polarizability mechanisms to compete. It is therefore hard to be predictive with a qualitative analysis for such systems; however, it is possible to understand the observed CD in light of the above comments.

3.3. Charged Systems. Ketones with C_{2v} carbonyl chromophores and charged chromophoric units (relatively near the carbonyl chromophore) will have their CD dominated by the r^{-3} charge-dependent mechanism of eq 4a. The CD of charged systems should be larger than for comparable neutral systems and exhibit an xy sector rule. The geometry of a system is usually readily determined, as is the charge, and the little experimental data that are available enable us to make a tentative prediction of the sign of $K_{\mathrm{mom}}{}^{\mathrm{ch}}$. Snatzke and Eckhard[19a] studied 4-equatorial and 4-axial –COOH (via the enantiomeric 2-axial form) substituted adamantones (cf. Figure 4) in both water and sodium

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(25) Bartlett, L.; Kirk, D. N.; Klyne, W.; Wallis, S. R.; Erdtman, H.; Thorén, S. *J. Chem. Soc. C* **1970**, 2678.

(26) Bull, J. R.; Enslin, P. R. *Tetrahedron* **1970**, *26*, 1525.

hydroxide solution. Let us first consider the theoretical predictions for the various mechanisms for the equatorial system. The dco CD for the –COOH chromophore is positive. $-C_z^{00}xyz$ and $C_y^{00}x(1-5y^2)$ are negative ($C_x^{00} \approx 0$), and $K_{\mathrm{mom}}^{\mathrm{dip}}$ is positive, so the dipolar CD is negative. The sign of the charge mechanism is opposite from that of $K_{\mathrm{mom}}^{\mathrm{ch}}$. Thus if we are to account for the positive CD of the 4-equatorial system in both NaOH and water, and the fact that the observed CD in NaOH (more dissociation so more charge contribution) was larger than in water, $K_{\mathrm{mom}}^{\mathrm{ch}}$ must be negative.

A negative $K_{\mathrm{mom}}^{\mathrm{ch}}$, however, fails to account for the negative CD of the axial compound in both solvents, since the dco CD is positive, the dipolar axial CD is positive (as for the F case above), and a negative $K_{\mathrm{mom}}^{\mathrm{ch}}$ results in a positive charge contribution. The magnitude is also a problem since the *r* dependence should in fact make this CD larger, rather than smaller, than the corresponding equatorial one. Solvent effects once again present a resolution of the dilemma. The potential for contributions from the solvent in these systems is even larger than in the previous β-axial systems considered, since the solvents can readily hydrogen bond to $-COO^-$ and –COOH. This introduces a large number of complicating factors. It is probable that, in its most stable association, the OH^- would project into a different quadrant from the COO^- and would thus generate a CD contribution of opposite sign from the COO^-. Similarly, it is likely that a hydrogen-bonded water molecule would make a net negative contribution.

4. Conclusions

It has been shown that for a wide variety of ketones in which a C_{2v} chromophore can be identified, the observed CD can be understood in terms of a perturbative mechanistic approach. In general, the isotropic polarizability dynamic coupling (dc) mechanism is dominant, so the CD reflects an octant rule geometry dependence on the positions of the inducing chromophores. However, before assuming a dco rule dependence, a number of questions must be answered. (i) Have all net-inducing chromophores been considered and their relative polarizabilities correctly accounted for? (ii) Have all potentially significant conformations of the system been considered? (iii) Are the net inducers positioned so that the geometry term *xyz* is not approximately 0? (iv) Are there no strongly dipolar or charge-inducing chromophores in the system? (v) Is the solvent completely randomly oriented with respect to the carbonyl chromophore? If the answer to any one of these questions is "no", then dco behavior is not necessarily to be expected as there will be either additional dco contributions (i, ii, and v), or other significant mechanisms (iii, iv, and perhaps v). For such situations the CD may still have the dco sign, but its magnitude will be inconsistent with that mechanism.

The neglect of solvent molecules about the carbonyl chromophore has been implicit in any theoretical work on carbonyl CD to date. The analysis in this paper suggests that there may be instances where this assumption is invalid. The β-axial substituent in such compounds as adamantones may create a "solvent hole" from which solvent molecules are excluded, resulting in a net solvent contribution of opposite sign from that of the dco contributions of the β-axial substituent. This hypothesis could be further investigated in a number of ways, including gas-phase CD experiments, molecular mechanics calculations on the solvent/β-axial carbonyl interaction, and further temperature-dependent studies. Theoretical investigations of the solvent structure about a carbonyl chromophore are in progress.

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Reaction of Singlet Oxygen with Organic Sulfides. A Theoretical Study

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Abstract: The intermediates in the reactions of singlet oxygen with H_2S and Me_2S have been calculated at Hartree–Fock, Møller–Plesset, and multiconfiguration levels of theory. A peroxy sulfoxide structure, which has been proposed as an intermediate in the photooxidation of organic sulfides, was found to be a stable intermediate, but the barrier for dissociation to reactants is calculated to be only a few kilocalories per mole. The infrared frequencies and intensities of this intermediate were calculated for the purpose of possible spectroscopic identification. A cyclic thiadioxirane, which also has been suggested as a possible intermediate, was found not to be a minimum on the potential energy surface. Large-scale MCSCF calculation shows that the peroxy sulfoxide is best described by a zwitterionic, not a biradical, structure. Calculated activation energies and overall reaction energies are found to require a very large basis set in order to give reasonable agreement with experimental results.

The reactions of singlet oxygen with simple organic sulfides have been studied extensively by several groups.[1-3a,4] The overall reaction is usually an oxidation of 2 mol of the sulfide by 1 mol of singlet oxygen to give 2 mol of the sulfoxide, although sulfones can be obtained under some conditions.[2] Trapping experiments suggest that the reaction proceeds via at least one intermediate, for which a peroxy sulfoxide structure has been proposed. Kinetic studies showed that the peroxy sulfoxide can rearrange in aprotic solvents to a second intermediate, suggested to have a cyclic thiadioxirane structure.[3] Sulfones can arise from further oxidation of the sulfoxides, but kinetic studies indicate that they can also be formed by unimolecular rearrangement of an intermediate (the

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(1) (a) For a review of photooxidation of sulfur compounds, see: Ando, W.; Takata, T. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC: Boca Raton, FL, 1985; Vol. 3, pp 1–117. (b) Ando, W.; Kabe, T.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (c) Foote, C. S.; Peters, J. W. In *XXIIIrd International Congress Pure and Applied Chemistry, Special Lectures*; Butterworth: London, 1971; Vol. 4, pp 129–154. (d) Ando, W.; Watanabe, K.; Suzuki, J.; Migita, T. *J. Am. Chem. Soc.* **1974**, *96*, 6766. (e) Cauzzo, G.; Gennari, G.; Re, F. D.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541. (f) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (g) Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, 4263. (h) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203. (i) Cauzzo, G.; Gennari, G.; Re, F. D.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541.

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