Conclusions

The semiempirical treatment (MNDO) applied to the lithiation of 1- and 2-naphthol reveals that mixed dimers of lithium naphthoxide–methyllithium having tetracoordinated lithium atoms do not "recognize" the proximal hydrogens. However, several degrees of agostic activation of the nearby hydrogens were evident when a ligand was withdrawn from the above fully coordinated mixed dimers. In particular, for the case of 1-naphthol, both hydrogens at C_8 and C_2 were clearly activated at this stage, as evidenced by all four indicators: C–H interatomic distances, C–H bond orders, LUMO 1s orbital coefficient of the hydrogen atoms, and H–Li distances. In contrast, the analogous mixed dimer resulting from 2-naphthol did not show significant (if any) agostic activation of the hydrogens at C_1 and C_3.

The subsequent lithiation was found to be exothermic only for 1-naphthol at C_8 (**1**→**8c**) but endothermic at C_2 (**1**→**9**). For 2-naphthol, lithiation is endothermic at both C_3 (**2**→**10**) and C_1 (**2**→**11**). The calculated enthalpies for these processes suggest that experimental factors, such as concentration and temperature, play a major role in the lithiation of naphthols. In fact, the calculated ΔG values obtained from ΔH and ΔS explain the apparent anomaly. Only lithiation of 2-naphthol at C_1 is now shown to be a clear-cut endergonic process ($T = 328$ K, $\Delta G = 6.4$ kcal/mol), thus providing a simple explanation for the observed regioselectivity in the lithiation of 2-naphthol.[31]

Remarkably, MNDO calculations predict that the π-type structures of the dilithio derivatives of naphthols having two ligands per lithium atom are significantly more stable than the conventional ones.[28] Unfortunately no experimental proof (or disproof) for this is available yet.

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Supplementary Material Available: Tables of Cartesian coordinates of the optimized molecular structures (14 pages). Ordering information is given on any current masthead page.

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(31) Note added in proof: Attention is called to a paper on the mechanism of other lithiations. Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191.

Theoretical Structure–Spectrum Relationships in the Circular Dichroism of Chiral Crown Ethers: Application to Chiral Pyridine-Substituted Crowns

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Abstract: A general sector function methodology is shown to be derivable from the GSR/ISP (generalized selection rule/independent systems perturbation) approach to the circular dichroism (CD) of achiral probe chromophore/chiral host systems and applied specifically to C_{2v} achiral probes. Coupled with an interpretative model encompassing physical assumptions regarding the electronic properties of the probe transitions and host system, the method is applied to a series of chiral pyridine-substituted crowns. The theoretical results are in good agreement with experimental behavior and suggest that the n → π^* pyridine transition is a sensitive probe of any species occupying the crown "holes" and thus of its association characteristics, whereas the L_a pyridine transition probes the crown backbone structure.

The structures of crown complexes in solution are a sensitive function of solution conditions. For crowns with chiral centers, circular dichroism (CD) constitutes a sensitive probe of solution conformation. Several experimental studies have been reported.[1,2] In particular, the attachment of an achiral aromatic substituent chromophore (A) to the chiral crown macrocycle (C_M) leads to an induced CD of the A transitions, which are in principle amenable to both a detailed experimental and theoretical analysis. The latter is fundamental to a proper definition of the relationship of the empirical CD behavior to the combined A/C_M structural relationships and hence to the internal structure of the macrocycle C_M. It is with such a detailed theoretical analysis of the CD of pyridine-substituted crowns that this paper is principally concerned.

The recent development of a fully symmetry-adapted formulation[3] of the well-known independent systems/perturbation (ISP) approach[4] to CD theory makes such a detailed theoretical analysis possible, thereby avoiding entirely the ambiguity implicit in postulation of qualitative or empirical "sector rules" and leading to analytic expressions for the CD that are always, in principle, capable of yielding both absolute sign and magnitude of the CD. The symmetry-adaptation procedure has its origin in the generalized selection rule (GSR) scheme for spectroscopic processes,[5,6] which provides a method of *analytically* symmetry-adapting perturbation expressions to the relevant symmetries of the interacting systems. The method has been implemented for both the cases of magnetic dipole allowed (mda)[3] and electric dipole allowed (eda)[7] transitions of A.

[†] Work completed while on Study Leave from the University of Sydney.

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In the present paper, the concept of sector functions is developed in the context of the GSR/ISP approach (Sector Rules and Sector Functions), and the general results for a C_{2v} A-chromophore system (probe) examined in some detail (GSR/ISP Analysis of a C_{2v} Probe). The results are then specifically applied, by using an interpretative model for simplifying both the probe and perturber response properties, to a purely theoretical analysis of the CD spectrum–structure correlations of a series of chiral pyridine-substituted crowns, which have been the subject of extensive empirical study (Interpretative Model for Pyridine Crown CD). The results are then compared to those of the experimental studies (Comparison with Experimental Data). Good agreement is obtained. Finally, the utility of the results for monitoring the association process of moities into the crown pockets is discussed (Conclusions).

Sector Rules and Sector Functions

The use of empirical sector rules has its origin in the CD spectroscopy of the carbonyl n → π* transition in chiral carbonyl compounds, for which the octant rule[8] has been put on a sound theoretical basis by Höhn and Weigang[9] using an independent systems/perturbation (ISP) approach and a detailed symmetry analysis specific to the carbonyl system. Detailed computational analyses have also been carried out testing the rule.[10] Schellman has also developed a set of symmetry rules for a range of A symmetries,[11] which have been used as the basis for a number of qualitative sector rule definitions. It has not always been fully appreciated that Schellman's "rules"[11] are rigorous only for the specific mechanistic case in which the perturbing field is a set of point static charges;[3] in spite of this, his rules have frequently been inappropriately applied as the basis of sector rules for transitions that become CD-active through the dynamic (dispersive) coupling between the probe and the chiral perturbing system. As will be discussed later, the CD of pyridyl crowns is dominated by mechanisms of the latter type, and thus the qualitative sector rules recently postulated on the basis of application of Schellman's rules to such systems are inappropriate.[2]

It is important to appreciate that the use of an ISP analysis is fundamental (and common) to any approach wishing to exploit the symmetries of the subsystems in order to give tractable analytic expressions for the relationship between the empirical CD and the A/C_M structural relationships. In an ISP analysis, the C_M system is represented by a set (C) of individually perturbing, nonexchanging local chromophores and the A system by a single chromophore, which also does not exchange with the residual C_M system. The induced CD of the A transitions is then developed as a sum over additive, separable contributions from each individual AC coupling, for which the Hamiltonian is partitioned in the form

$$H = H_A + H_C + V_{AC} \qquad (1)$$

where H_A is the Hamiltonian of subsystem A, ditto H_C, and V_{AC} is the Coulomb interaction operator of all charges on A with all those on C. The isolated chromophore solutions (solutions of H_A and H_C, respectively) are used to form product functions as a basis for the solution of the full Hamiltonian. Neglect of exchange (implicit in an AC-product basis in which electrons are uniquely identified with the A or C system), expansion of V_{AC} as a multipole expansion about the AC origins, and a perturbative analysis in terms of V lead to the usual ISP expressions, which are fully given elsewhere.[3]

The residual and nontrivial difficulties implicit in a *practical* implementation of the ISP methodology, and also the basic factors discriminating between various applications of the ISP results in the literature, are the choice of which perturbation terms ("mechanism") dominate for a particular type of A (probe) transition, the criteria for that choice, and the symmetry analysis of the chosen terms. (In some cases, the actual chromophore definitions may also vary, but this factor is more relevant to metal-complex systems.) These factors are in fact inextricably related and have been rigorously addressed in the following way.

The ISP CD strength for a given A transition and a given C perturber may always be written as a sum of terms, each having the symbolic form

$$\mathrm{R} \sim k\, f_A(xyz)\, f_C(x'y'z')\, F_{AC}(xyz \Leftrightarrow x'y'z')r^{-n} \qquad (2)$$

where k is a scalar absorbing any constants and energy denominators, r is the separation of the AC origins, (xyz) and $(x'y'z')$ are A-fixed and C-fixed coordinate systems defined at the origins of A and C, respectively, $f_A(xyz)$ is the *A-response function* (e.g., a transition moment product involving only A states and A-centered multipole operators, or a tensor formed from such terms), ditto f_C (the *C-response factor*) on C, and F_{AC} (the *geometrical* coupling factor) is a function of the relative orientation and disposition of the A,C-coordinate systems. In practice, the factors f_A, f_C, and F_{AC} are interconnected by tensorial products (for which their relative order may be important), but the above simplified symbolic form suffices for the general arguments that follow.

The dominant factor leading to simplification of such expressions is the effective symmetry of the A system (G_A). (We retain here the general case for which the C_M system has no symmetry, although if such symmetry is present, it may also be incorporated in the manner described for A below.) We choose the $(x'y'z')$ system to be parallel to the (xyz) system of A and centered on the C origin. The A symmetry may be incorporated by using the GSR (generalized selection rule) scheme, specifically developed to effect an *analytic* symmetry simplification of such general perturbative products.[5] If G_A has the set of h_A operations (Ξ_A), and

$$P^{\circ}{}_A = h_A{}^{-1}\textstyle\sum_{\Xi}\Xi_A \qquad (3)$$

then, using also the particular choice of the $(x'y'z')$ system for C, we have

$$\mathrm{R}(G_A) \sim k\, f^{\circ}{}_A(xyz)\, f^{\circ}{}_C(x'y'z')S(x_Cy_Cz_C)r^{-n} \qquad (4)$$

where

$$f^{\circ}{}_A(xyz) = P^{\circ}{}_A f^{\circ}{}_A \qquad (5)$$

The P° act directly on the operator products, and explicit analytic expressions for general tensorial products of arbitrary order have been derived,[6] as well as applied to a general symmetry adaptation of perturbative ISP expressions.[3] It is important to appreciate here that the effect of each P° is a *complete* symmetry adaptation, both eliminating rigorously vanishing terms and effecting the transformation to the corresponding expression in terms of symmetry invariants. This leads to the elucidation of the term with the dominant (i.e., smallest n) radial dependence. Finally, the particular choice of the C system reduces the geometrical coupling factor to a *positional sector function* $S(x_Cy_Cz_C)$, a function only of the coordinates $(x_Cy_Cz_C)$ of the C origin in the A system.

A conventional sector rule is a partitioning of space based on the A symmetry such that the sign of the induced CD contribution from a perturbing group C depends directly on the sector in which the origin of C lies. In the above analysis, the factor encapsulating this dependence (*for a given A transition* and hence constant A-response function) is the *positional sector function S*. Thus, a conventional sector behavior (which will be characteristic of the nature of the A transition and may be different for different transitions) will only be expected if the perturbers of interest are *all* representable by scalar C-response functions; i.e., which are independent of the choice of the A system, and thus *xyz*. In this case, the contribution to the CD for this particular A transition from each C perturber depends only on the scalar C function and the positional sector function appropriate to that mechanism and symmetry. A more general case occurs when the perturber response function has the nonscalar form

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$$f^\circ_C(x'y'z') = g^\circ_C s_C(x'y'z') \tag{6}$$

where g°_C is a scalar, but $s(x'y'z')$ is a perturber *orientation sector function*. In this case, the CD depends on the *product* of the appropriate positional and orientational sector functions.

In order to see when these different types of behavior may be expected, we note that the induced CD may be of two general types. Noting that CD requires an electric and magnetic coupling to the field, the two general classifications of mechanisms may be effected on the basis of the criterion of whether the magnetic response has its origin in an intrinsic magnetic transition moment on A or C (intrinsic magnetic mechanisms) or it arises from a magnetic coupling due to two suitably directed electric transition moments on A and C (coupled-oscillator mechanisms). These two classes of mechanisms differ substantially in their geometric properties.

For the intrinsic magnetic mechanisms in which the magnetic dipole transition moment of the A transition is exploited, a representation of C by its isotropic (scalar) polarizabilities frequently leads to the dominant CD terms. In such cases, conventional sector behavior occurs, and a single conventional sector rule may be expected to emerge from empirical studies for which this mechanism applies. For coupled-oscillator mechanisms, however, such a representation of C does not (at least to first order in the ISP expressions) lead to CD, as the coupling between the AC electric moments is dependent not only on their separation, but also sensitively on their relative orientation. This leads to the typical *combined sector behavior* characteristic of a product of the positional and orientational sector functions. The properties of the positional and orientational sector functions may be investigated separately, as we shall see later, leading to a general sector function approach applicable to all mechanisms.

GSR/ISP Analysis of C_{2v} Probes

The CD spectroscopy of the pyridine-substituted crowns may be expected to be relatively complex, especially for conformationally variable crowns. Even for a conformationally rigid crown, there are many potential perturbing units and mechanisms. It is important, therefore, to proceed in three distinct stages, so that the potential complexity arising from competing mechanisms for a fixed conformation is clearly delineated from the empirical complexity implicit in potential conformational equilibria. The first stage is the clear definition of all the dominant mechanisms in the context of a GSR/ISP analysis for each potential transition in a C_{2v} achiral chromophoric system. This GSR/ISP analysis is the least controversial stage and is the stage we shall address separately in this section as the results transcend the particular applications to pyridyl crowns discussed in later sections. The second stage may be referred to as the establishment of an *interpretative model*, in which certain *probe* transitions of the achiral chromophore are selected, so that each is assumed to appear in the CD through a single dominant mechanism and perturbed through a characteristic *dominant* perturber. The interpretative model is established through criteria gleaned both from the theoretical analysis and from the absorption and chemical characteristics of the chromophores in the system. A particular interpretative model can be inappropriate without invalidating the GSR/ISP model. However, it is through such an interpretative model that the CD may be developed as a tractable function of the conformation, so that the comparison of empirical and theoretical CD behavior may be used as a structural probe, constituting the third stage. The development of the interpretative model is dependent on the particular nature of the system of interest and will be discussed in later sections for the case of pyridyl crowns.

We consider a general A system of intrinsic C_{2v} symmetry, with the intrinsic (xyz) system defined such that the z axis is directed along the C_2 axis, the y axis in the plane (if the system is a planar aromatic, for example), and the x axis out-of-plane. A number of symmetry-allowed transitions are possible for a C_{2v} system. An A_2 transition is of pure magnetic dipole character, with magnetic z polarization; an A_1 is of pure electric dipole character, with electric polarization along the z axis. B_1 and B_2 transitions are both electric and magnetic dipole allowed. Consistent with the achirality of the C_{2v} chromophore, however, a B_1 transition is magnetically y-polarized, electrically x-polarized, and vice versa for a B_2 transition. For a C_{2v} system in general, therefore, an A_2 transition may attain CD activity through an intrinsic magnetic mechanism exploiting its intrinsic z magnetic transition moment. This, for example, leads to the characteristic octant rule behavior of the induced CD of the carbonyl n → π^* transition in chiral structures.[8,9] An A_1 transition, because it is electric dipole allowed, is more likely to attain its CD activity through a coupled oscillator mechanism.[12-14] For B_1 and B_2 transitions, both mechanisms are possible and may contribute additively.

In the determination of the GSR/ISP CD for a C_{2v} symmetry system, the achiral group symmetry is sufficiently low to ensure dominance of the first-order terms in V. Thus, it is sufficient to consider only the excited states $|i\rangle$ on A, $|u\rangle$ on C, with isolated chromophore transition energies ϵ_i, ϵ_u relative to the ground states (both denoted $|0\rangle$ with implicit A or C labeling), respectively. If the purely static effects and any intrinsic magnetic moments on the *individual perturber* chromophores are neglected, then magnetic dipole allowed transitions of A may attain CD activity through the *first-order dynamic coupling* (*dc*) terms and electric dipole allowed transitions of A through the *first-order coupled oscillator* (*co*) terms. (Although such assumptions are characteristic of the interpretative model stage, they are of relatively broad applicability, and we simply restrict our consideration to the general class of systems for which this is the case.) We consider these in turn.

Magnetic Dipole Allowed Transitions: C_{2v}. The full GSR simplification of the first-order dynamic coupling terms have been discussed in detail elsewhere,[3] and we consider here exclusively the leading r^{-n} terms for $G_A = C_{2v}$, and with each chromophore of the crown individually represented by its isotropic response functions at the respective origin.

Let α $(=x,y,z)$ denote the magnetic polarization of the A transition such that

$$m_\alpha{}^A(i,0) = \langle i|m_\alpha{}^A|0\rangle \tag{7}$$

where the magnetic moment operator $\mathbf{m}$ is given by

$$\mathbf{m} = (e/2m_e)\ell \tag{8}$$

ℓ is the angular momentum operator, e the electronic charge, and m_e the electronic mass. m_α is therefore the α component of the intrinsic magnetic dipole operator $(\mathbf{m}^A)$ of A defined at the A origin. The electric moment operators of A defined at the same origin may be written in the form

$$\mu_\alpha{}^A = \textstyle\sum_a e_a \rho_{\alpha a}; \qquad Q_{\alpha\beta} = \textstyle\sum_a e_a \rho_{\alpha a}\rho_{\beta a} \tag{9}$$

where e_a is the charge on particle a of the A chromophore and $\rho_{\alpha a}$ the α component of its position relative to the A origin. Intrinsic electric moment operators relative to the C origin of the C-chromophore charges may be analogously defined, either with respect to components in a general C-fixed $(x'y'z')$ system (denoted α') or with respect to the specific (xyz) system defined earlier [i.e., the A system (xyz) but translated to the C origin], which we denote by α. The unit position vector of the C origin with respect to that of A expressed in the (xyz) A system may be defined as

$$\hat{\mathbf{r}} = (X,Y,Z) = (x_C,y_C,z_C)/r \tag{10}$$

In the work that follows, the A moments refer exclusively to the 0 → i transition and the C moments to the 0 → u transition, so that these arguments may be left understood. Note that the state ordering for electric transition moments is irrelevant, but that of the magnetic moment is crucial, as $\langle i|m_\alpha{}^A|0\rangle = -\langle 0|m_\alpha{}^A|i\rangle$. We shall consider the magnetic transition moment as referring implicitly to the element defined in eq 7. The CD strength arising

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from the *dc* mechanism adapted to $G_A = C_{2v}$ symmetry may then be written in the form

$\alpha = x$; B_2 symmetry:

$$R_x(dc) = 2[\epsilon_u/(\epsilon_u^2 - \epsilon_i^2)][\mu^C \cdot \mu^C]\ \mathrm{Im}[m_x^A \mu_y^A][XY]r^{-3} \quad (11)$$

$\alpha = y$; B_1 symmetry:

$$R_y(dc) = 2[\epsilon_u/(\epsilon_u^2 - \epsilon_i^2)][\mu^C \cdot \mu^C]\ \mathrm{Im}[m_y^A \mu_x^A][XY]r^{-3} \quad (12)$$

$\alpha = z$; A_2 symmetry:

$$R_z(dc) = 10[\epsilon_u/(\epsilon_u^2 - \epsilon_i^2)][\mu^C \cdot \mu^C]\ \mathrm{Im}[m_z^A Q_{xy}^A][XYZ]r^{-4} \quad (13)$$

There are effectively five distinct factors in each of these expressions, some of which are also common to the *co* CD to be discussed later. The first is the *energy factor*, which will generally favor perturber transitions that are as close as possible (energetically) to that of the achiral chromophore transition of interest. In practice, we are generally interested in achiral groups for which $\epsilon_i < \epsilon_u$, for which the overall energy factor is positive. Noting in addition that each of the above expressions is implicitly summed over all states $|u\rangle$ of the perturber, it is possible to effect a broad characterization of a perturber group as a *quantum perturber* if it has a low energy transition for which the energy factor leads to its dominance in the sum, and as a *classical perturber* if many states of C contribute with a roughly constant energy term. This leads to the *C factor* (the second factor in brackets) being simply the relevant dipole strength for a quantum perturber or combining with the energy term (the first factor) to yield an effective polarizability for a classical perturber. The third factor is the *A* factor, which depends purely on the properties of the relevant A transition and is in principle calculable. (We shall consider its detailed calculation later.) It is important to appreciate that the form of the *A factor does not itself define sector behavior*, as it is a scalar defined purely in the coordinates of the A system and makes no reference to the geometry of the perturbing system. The latter is implicit in the fourth factor, the *positional sector function*. Finally, the fifth factor is the *r* dependence. The latter two factors combine in defining the *geometric structural factors*, but the first two factors define the *perturbing response functions* that are responsible for the CD induction; i.e., the C-response functions define what the perturber is represented by at its origin (in this case, a polarizability-type scalar) and the geometrical structural factors the purely geometrical aspects associated with how this representation acts at A.

We have purposely developed the above discussion in somewhat general terms in order to apply it as a basis for discussing other mechanisms as well as the *dc* CD contributions given above, for it highlights the fact that the intrinsic magnetic and coupled oscillator mechanisms or even different A transitions appearing through a similar class of mechanisms may probe quite different parts of the structure (through the geometrical factors) and quite different aspects (C-response functions) of the structure. In the case of the *dc* CD mechanisms listed above, the dominant contributions for all polarizations depend on the *same* C-response function (of the form of a polarizability) and, specifically, on the diagonal terms of the polarizability. Thus, in many cases, it is sufficient to use the isotropic polarizability of the perturbers. However, the geometrical aspects are quite sensitive to the magnetic polarization. For example, for magnetically *z*-polarized transitions, the well-known octant dependence[9] is implicit in the positional sector function $[XYZ]$, with a radial dependence of r^{-4}. However, the other two polarizations have a slower *r* dependence, a *quadrant* positional sector function $[XY]$, and also distinctly different A factors.

We may exploit these differences in deducing a general set of rules for the *dc* CD of a C_{2v} chromophore, which find a direct practical expression later in the applications to pyridyl crowns. If we define A* as the chromophore obtained by reflecting A *only* (i.e., not C_M) in the *xy* plane through the A origin and retain the *same* coordinate system for both the A/C_M and the A*/C_M systems, then the following general rules may be directly deduced from the above expressions (with $\epsilon_u > \epsilon_i$):

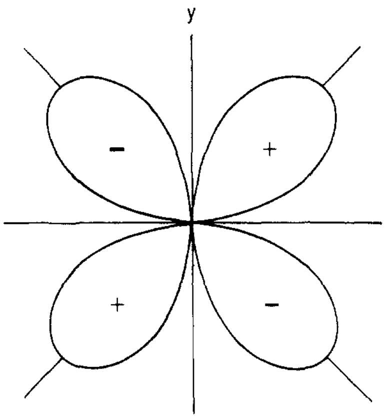

Figure 1. Sector function *XY* representing pure quadrant behavior. The axes represent critical minima, whereas the lines bisecting the quadrants represent the critical maxima.

1. Magnetically x- and y-polarized transitions will (i) manifest quadrant behavior, with an absolute sign determined by that of the respective A factors ($Im[m_x^A\mu_y^A]$, $Im[m_y^A\mu_x^A]$ *respectively*), *(ii) maintain their relative intensities and sign for conformational changes in the* C_M *system, (iii) have an* r^{-3} *dependence of AC separation, and thus may be expected to be stronger than magnetically z-polarized transitions, and (iv) both reverse their sign for the* A^*/C_M *system (relative to that of the* A/C_M).

2. Magnetically z-polarized transitions will (i) manifest octant behavior with the absolute sign determined by that of the A factor ($Im[m_z^AQ_{xy}^A]$), *(ii) have an* r^{-4} *dependence, and (iii) retain their sign for the* A^*/C_M *system (relative to that of the* A/C_M).

The comparisons between the A/C_M and A*/C_M systems derive from effecting the *xy* plane reflection on the operator product, which is readily shown to lead to the equivalent result as the operation on the wave functions of A.[15] In practice, an additional translation of the A-reflected system along the *z* axis may be required to yield a real A*/C_M structure, in which case the positions of the C origins in the A-fixed system will also be modified, leading to a parallel modification of the ideal behavior (no translation) of 1iv and 2iii.

It should be noted that we have explicitly discussed the sector behavior not in terms of sector *rules*, but in terms of sector *functions* giving the full orientational dependence. For example, the quadrant sector functions are plotted in Figure 1. Note that it is not sufficient that a group lie just outside a node; it must lie well outside, with the maximum at 45° to either axis. It is important therefore to plot the full sector behavior for all mechanisms and not merely speculate on the positions of the nodal planes. We shall in fact see that the positions at which the sector functions have a maximal magnitude (the *critical maxima*) play an equally important selective role as that of the nodes (the *critical nodes*).

A final point worthy of some mention here is that the dominance of the *dc* CD mechanism relies, for the magnetically *x*- and *y*-polarized transitions, on a relatively large magnetic component and small electric component of the A transition. (Otherwise the *co* CD mechanism may become competitive.) Thus, it is most likely to dominate the CD of transitions that involve rotations of directed orbitals (p, d) to orbitals of the same type (but different orientation) on a single atomic center, such as the n → π* transitions of organic chromophores, or the d → d transitions of metal complexes. For a C_{2v} system derived from benzene, the π → π* transitions are unlikely to involve appreciable magnetic character, especially if the parent transition has no such character in benzene. Such aromatic π → π* transitions may generally be expected to become CD active through the mechanisms discussed below.

Electric Dipole Allowed Transitions: C_{2v}. Whenever a transition appears with relatively strong intensity in normal absorption *and*

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[15] Schipper, P. E. *Chem. Phys.* **1979**, *44*, 261.

has no or weak magnetic character (in the sense discussed in the previous section), it is most likely to gain CD activity through the direct exploitation of its electric transitional dipole character and, in particular, the coupled oscillator mechanism.[12-14] Weigang[14] has discussed "amplified" sector rules arising from a full analytic analysis of this mechanism. In the present work, however, the analysis is developed in terms of axis system choices consistent with those used in the parallel analysis of the magnetic mechanism, so that the positional sector functions are expressed in terms of identical Cartesian variables in both cases and clearly separated from the orientational sector functions. The full expression for the first-order coupled oscillator (*co*) contributions may be written in the convenient form[7]

$$\mathrm{R}(co) = \hbar^{-1}[\epsilon_i\epsilon_u/(\epsilon_u{}^2 - \epsilon_i{}^2)]\tilde{T}^{\mathrm{A}}{:}\tilde{T}^{\mathrm{C}}r^{-3} \qquad (14)$$

where

$$\tilde{T}^{\mathrm{A}}{:}\tilde{T}^{\mathrm{C}} = \textstyle\sum_{\alpha\beta}T_{\alpha\beta}{}^{\mathrm{A}}T_{\alpha\beta}{}^{\mathrm{C}} \qquad (15)$$

and

$$\tilde{T}^{\mathrm{A}} = \boldsymbol{\mu}^{\mathrm{A}}\boldsymbol{\mu}^{\mathrm{A}}, \quad \tilde{T}^{\mathrm{C}} = -\boldsymbol{\mu}^{\mathrm{C}}[\mathbf{r}\times\boldsymbol{\mu}^{\mathrm{C}}] + 3(\boldsymbol{\mu}^{\mathrm{C}}\cdot\hat{\mathbf{r}}^{\mathrm{C}})\hat{\mathbf{r}}[\mathbf{r}\times\boldsymbol{\mu}^{\mathrm{C}}] \qquad (16)$$

The symmetry adaptation of the above expression proceeds through noting that the A tensor simplifies under C_{2v} to a matrix with only one nonzero element for each of three possible electric polarizations of the A-chromophore transition; viz. for the electrically α-polarized transition, only $T_{\alpha\alpha}{}^{\mathrm{A}} = (\mu_\alpha{}^{\mathrm{A}})^2$ is nonvanishing, and

$$\mathrm{R}_\alpha(co) = \hbar^{-1}[\epsilon_i\epsilon_u/(\epsilon_u{}^2 - \epsilon_i{}^2)](\mu_\alpha{}^{\mathrm{A}})^2T_{\alpha\alpha}{}^{\mathrm{C}}r^{-3} \qquad (17)$$

where

$$T_{\alpha\alpha}{}^{\mathrm{C}} = -\mu_\alpha{}^{\mathrm{C}}[r_\beta\mu_\gamma{}^{\mathrm{C}} - r_\gamma\mu_\beta{}^{\mathrm{C}}] + 3(\boldsymbol{\mu}^{\mathrm{C}}\cdot\hat{\mathbf{r}}^{\mathrm{C}})\hat{r}_\alpha[r_\beta\mu_\gamma{}^{\mathrm{C}} - r_\gamma\mu_\beta{}^{\mathrm{C}}] \qquad (18)$$

and $(\alpha\beta\gamma)$ are a cyclic permutation of $(x'y'z')$. It is possible to expand this product explicitly by defining $(AB\Gamma)$ as the corresponding permutation of the unit radial vector (XYZ). Writing

$$\boldsymbol{\mu}^{\mathrm{C}} = |\boldsymbol{\mu}^{\mathrm{C}}|\boldsymbol{\rho}^{\mathrm{C}},\ \boldsymbol{\rho}^{\mathrm{C}} = (\alpha,\beta,\gamma), \quad t_{\alpha\alpha}{}^{\mathrm{C}} = (r|\boldsymbol{\mu}^{\mathrm{C}}|^2)^{-1}T_{\alpha\alpha}{}^{\mathrm{C}} \qquad (19)$$

such that

$$\mathrm{R}_\alpha(co) = \hbar^{-1}[\epsilon_i\epsilon_u/(\epsilon_u{}^2 - \epsilon_i{}^2)](\mu_\alpha{}^{\mathrm{A}})^2(\mu^{\mathrm{C}})^2t_{\alpha\alpha}{}^{\mathrm{C}}r^{-2} \qquad (20)$$

it follows that the $t_{\alpha\alpha}{}^{\mathrm{C}}$ may be expanded in the explicit form

$$t_{\alpha\alpha}{}^{\mathrm{C}} = \alpha\gamma[-B + 3A^2B] \qquad (21)$$

$$+\alpha\beta[\Gamma - 3A^2\Gamma] \qquad (22)$$

$$+\beta\gamma[3AB^2 - 3A\Gamma^2] \qquad (23)$$

$$+\beta\beta[-3AB\Gamma] \qquad (24)$$

$$+\gamma\gamma[3AB\Gamma] \qquad (25)$$

$$= \textstyle\sum_\nu s_\alpha{}^{(\nu)}(\alpha\beta\gamma)S_\alpha{}^{(\nu)}(AB\Gamma) \qquad (26)$$

In the above expression, the energy factor behaves in a manner similar to that for the *dc* CD mechanism, leading to a broad partitioning into quantum and classical perturbers. The C factor here, although apparently related to the dipole strength of the C perturber, also contributes to the combined structural factor *t* through the orientational sector function *s*, from which it is apparent that the crucial consideration is the *anisotropy* of the perturber, a point we return to later. The dependence on the A factor is simply proportional to the oscillator strength of the relevant A transition, a convenient factor allowing for the expectation that the magnitude of *co* CD effects roughly parallels intensities in normal absorption. The most interesting aspect, however, is the dependence, through the *t* factor, on the orientation and position of the perturber, an aspect that we shall consider in some detail.

It is interesting to note that each contribution in the expression 21–25 (i.e., each contribution labeled by ν in eq 26) has the combined sector behavior discussed earlier and thus will not generally be expected to reduce to conventional sector behavior. The quantity in brackets $[=S_\alpha{}^{(\nu)}(AB\Gamma)]$ defines the dependence on the *position* of the origin of the C perturber relative to that of the A origin (the positional sector function). The prefactor $[=s_\alpha{}^{(\nu)}(\alpha\beta\gamma)]$ defines the dependence on the *orientation* of the perturbing C moment in terms of an A system fixed at the C origin (the orientational sector function). Free rotation of the C perturber about its own origin will lead to such contributions rigorously vanishing, so that isotropic polarizability representations of C cannot (in first order) lead to *co* CD. This is also implicit in the anisotropic (nondiagonal or difference diagonal) form of the individual orientational sector functions. It follows that it is the *directionality* of the C moments that is crucial in leading to a finite *co* CD. For a quantum perturber, this directionality is generally implicit in the fact that individual transitions have an effective directional polarization for nondegenerate transitions. For a classical perturber, it requires certain polarizations to contribute more heavily to the overall transition sum. We may generally represent a classical perturber for a *co* CD analysis as a bond with an *effective* bond moment along the bond with an *effective* transition energy. The overall C-response function is therefore expressed in terms of the set of off-diagonal elements of an effective polarizability tensor expressed in the A coordinates and, thus, involves a distinctly different type of response function than that implicit in the *dc* CD mechanism. The *two mechanisms therefore yield different and complementary information about the perturbing system.*

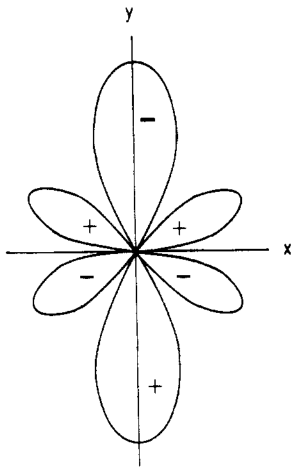

Figure 2. Plot of the positional sector function $[-Y + 3X^2Y]$.

A seemingly complicating factor in analyzing the *co* CD is the potential contribution to the combined *t* factor from *several* of these terms, *each* having its own characteristic combined sector behavior. In this respect, the *co* CD appears considerably more complex than that expected for the *dc* mechanism. It is important to appreciate that this complexity is an intrinsic feature of the *co* CD mechanism and stems ultimately from its dependence on both orientation and position of the perturbing C moment. The question arises, however, as to how the structural factors for the *co* CD contributions may be determined in a practical sense, especially when a large number of perturbers are present. Two factors may aid such an analysis. The first is the potential dominance of quantum perturbers, in which the energy selection assures a high anisotropy by selecting a single dominant transition dipole. An equally potent but more general selector is the geometry of the perturbing system itself. For example, the positional sector functions for all possible *co* contributions may be represented by three plots, shown in Figures 2–4. These functions show distinct directional behavior characteristic of each particular *co* contribution, with the characteristic critical maxima and nodes at quite different positions. All the positional sector functions may be obtained by inserting the relevant axes and multiplying by −1 where the required function has the sign opposite to that plotted. (For the $3AB\Gamma$ terms, only the $3AB$ part is plotted for convenience, as a full plot would require a three-dimensional

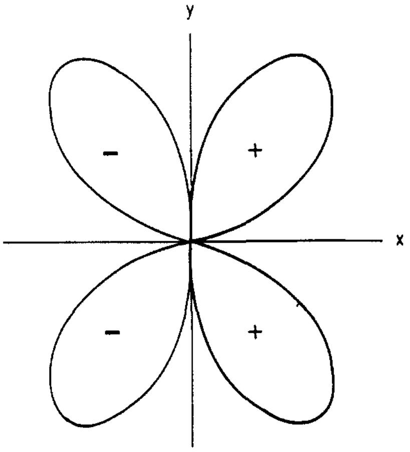

Figure 3. Plot of the positional sector function $3XY^2$.

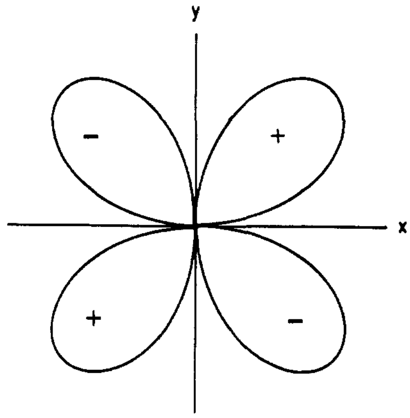

Figure 4. Plot of the positional sector function $3XY$.

representation.) Note that the maximum of the first plotted positional sector function lies precisely at a node of the second, and vice versa. It is this sort of behavior (also discussed by Weigang[14]) that will frequently lead to a dominance of just a few terms. Coupled with the r^{-2} factor, the dominant perturbers in these directions can then be determined and the relevant orientational sector functions examined.

All in all, the CD expected through the *co* mechanism is critically system-dependent, and the above analysis should serve as a warning that the simple conventional sector behavior characteristic of the CD of strongly magnetic dipole allowed transitions is neither expected nor desirable in the sense that the *co* CD will therefore yield quite different structural information. The above analysis also demonstrates in a general way why there have emerged a range of "apparent" sector rules for $\pi \rightarrow \pi^*$ transitions of aromatic chromophores, which are most likely to attain CD activity through the *co* mechanism. For example, perturbers lying at critical maxima of a single positional sector function will often lead to a dominance of the relevant *t* term, so that the combined sector function product mimics an *overall* Cartesian function formed from both terms, and thus an *apparent* conventional sector rule. However, perturbers lying at a critical maximum of *another* positional sector function (and thus acting through quite a different orientational sector function) will mimic a different *apparent* conventional sector function. Thus, a multiplicity of "empirical" sector rules may be expected for such systems, each appearing to be valid for a given class of perturbers. This is indeed the case on examination of the literature.[16-18] For $n \rightarrow \pi^*$ transitions, for which conventional sector behavior is theoretically expected, such multiplicity is not as prevalent, and even apparent "breakdowns" of the sector behavior may be ascribed to an oversimplistic analysis of the perturbing system;[19] i.e., in our terminology, to an inappropriate representation, in the interpretative model, of the perturbing system.

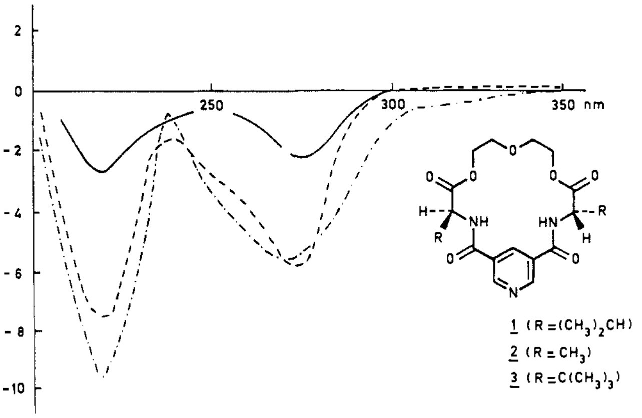

Figure 5. Structure and circular dichroism of **1**–**3**. All spectra in ethanol. **1** (---), **2** (—), and **3** (-·-). The Z axis is directed along the symmetry axis of the pyridine (positive pointing upwards on the page), with the Y axis in the aromatic plane (positive pointing to the right), and the X axis perpendicular to the page.

Interpretative Model for Pyridine Crown CD

In the previous sections, the GSR/ISP expressions for a C_{2v} probe have been determined in a general way for those mechanisms involving a transitional dipolar response of the perturbing system. In application of the expressions to pyridine crowns, it is desirable to simplify these expressions further through the mediation of an interpretative model. It is important to appreciate, as mentioned earlier, that the interpretative model encapsulates the *additional* assumptions peculiar to a given achiral probe/chiral perturbing system combination in order to cast the results in a practically usable and theoretically tractable form; it will therefore not necessarily enjoy the broad transferability of the more general GSR/ISP results between systems of similar *symmetry*. Such an interpretative model may, however, retain maximal transferability between similar *chemical* systems if the assumptions pertaining to the achiral probe (A) are, as far as is practicable, clearly delineated from those defining the dominant perturbers. We therefore consider the representation of the achiral probe first and then return to simplification of the perturbing system.

Probe Transitions of the Pyridyl Chromophore. The isolated pyridine chromophore has three transitions in the accessible 300–200-nm range, which are, in order of increasing transition energy, (i) the ($n \rightarrow \pi^*$) *n transition* of B_1 symmetry appearing as a shoulder (at ~275 nm) in normal absorption[20] on (ii) the ($\pi \rightarrow \pi^*$) L_b *transition* ($\epsilon \simeq 2500$) of B_2 symmetry (at ~250 nm), followed by (iii) the more intense ($\pi \rightarrow \pi^*$) L_a *transition* ($\epsilon \simeq 7400$) of A_1 symmetry (at ~225 nm).[21]

Of these, the L_a *transition* (A_1) alone is electric dipole allowed and magnetic dipole forbidden and, thus, must become CD active through exploiting its electric dipole character, i.e., for the mechanisms considered here, solely through the *co* mechanism. It is therefore a reliable probe of perturbers that can lead to *co* CD. The intrinsic magnetic transition moment of the *n transition* may be expected to be large, so that it is most likely to become CD active through the *dc* CD mechanism and will therefore be taken to be a probe of potential *dc* perturbers. The L_b *transition* may occur through both mechanisms, but as the corresponding transition is magnetic dipole forbidden in benzene, it is most likely to exploit the *co* mechanism. In any case, its significantly smaller *co* CD (relative to that of the L_a transition), significant interference from the surrounding n and L_a CD, and potential overlap with the amide carbonyl $n \rightarrow \pi^*$ CD[22] suggest that it is the least

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(16) de Angelis, G. G.; Wildman, W. C. *Tetrahedron* **1969**, *25*, 5099.
(17) Snatzke, G.; Ho, P. C. *Tetrahedron* **1971**, *27*, 3645.
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(19) Rodger, A.; Rodger, P. M. *J. Am. Chem. Soc.* **1988**, *110*, 2361.
(20) Schipper, P. E.; Nordén, B. *Chem. Phys. Lett.* **1979**, *67*, 99.
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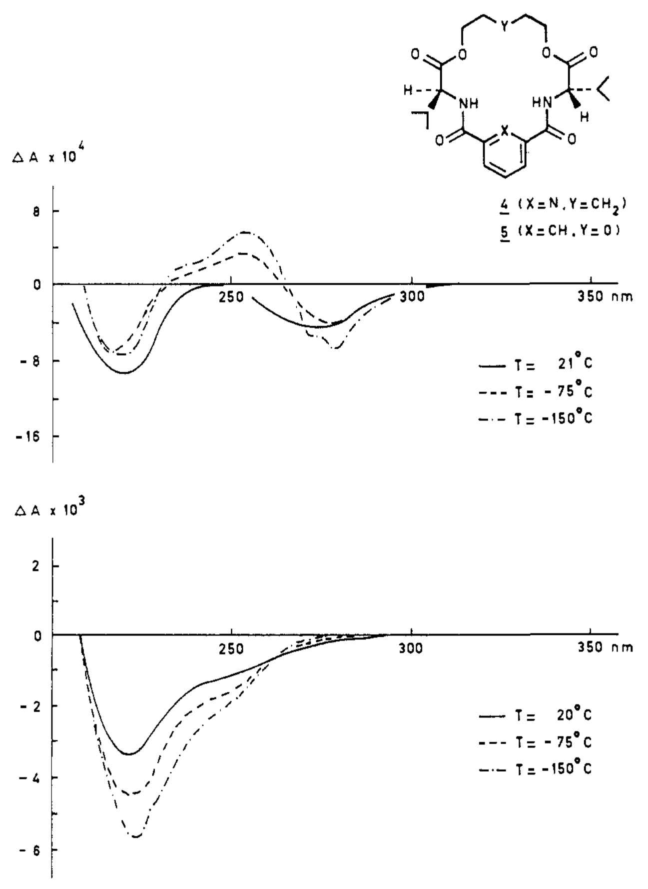

Figure 6. Structure and circular dichroism spectra (in ethanol) of **4** and **5**. (Coordinate system as for Figure 5.) The effect of temperature is also indicated.

appropriate for use as a probe transition. We shall concentrate therefore on the CD of the n and L_a transitions as the most suitable direct probes of the structure; i.e., as the *probe transitions*.

Simplifications of Perturbing System. We consider the particular perturbing system present in the series of pyridine crowns **1**–**5** illustrated in Figures 5 and 6, which form the basis of our practical applications. These have been the subject of recent spectroscopic studies[1] and may be considered as having structures based on the experimentally determined structure of **1** with a pentamethylene chain in the bridge rather than the 3-oxapentane.[1] Of these, only the inverted crown **4** may be expected to deviate significantly from the basis structure. From the collective data (as justified below), the following interpretative model may be defined: (*i*) *the L_a transition derives its CD from a co coupling with the amide carbonyls as the dominant perturbers*; (*ii*) *the n transition derives its CD from a dc coupling with an interplay between two perturbing systems, which may be defined relative to the four XY quadrants* (*in reference compound* ***1***); (*a*) *the R groups attached to the amide nitrogen* (*$XY < 0$*) *and* (*b*) *the solvent molecules in the asymmetrically disposed pockets in the $XY > 0$ quadrants*. Justification of this model has its basis in the following experimental features.

The basis structure[1] indicates that the amide carbonyls are skewed out of the pyridine plane into the $XY > 0$ quadrants, with the amide R groups strongly directed into the opposing quadrants, and with large residual pockets in the $XY > 0$ quadrants. The UV spectra[1] indicate that the pyridyl chromophore features dominate the region energetically below 225 nm, with the amide carbonyl $\pi \rightarrow \pi^*$ appearing at ~200 nm. Strong pyridyl/amide carbonyl conjugation is precluded by the skewed geometry (and supported by the integrity of the pyridyl part of the spectrum), so that the L_a band at ~225 nm may be expected to form a near-degenerate coupled oscillator system with the amide carbonyl transition at 200 nm, leading to a strong L_a *co* CD. The proximity in energy of these two transitions and the spatial proximity of the two chromophores therefore suggests that any other perturbations may be neglected for the L_a band. We will therefore analyze the CD for this transition in this way.

For the n transition, it is apparent (as discussed in detail below) that the *dc* CD is noded at $X = 0$, and thus only out-of-plane perturbers will be significant. The amide R and carbonyl perturbers will therefore be potentially significant. For an isolated molecule as represented by a molecular model, they will be the only perturbers we need to consider simply on the grounds of spatial proximity. In a solvent, however, any *asymmetrically diposed pockets in the model* are filled with polarizable solvent, and *must* be included as potential contributors to the *dc* CD. The role of such solvent pockets has been previously discussed in the context of apparent "failures" of the carbonyl $n \rightarrow \pi^*$ octant rule using the GSR/CD expressions.[19] This feature becomes particularly significant in chiral crowns, as we shall see.

Finally, the interpretation of the CD relies on its dominance by the pyridyl transitions in the region energetically below 225 nm. The carbonyl $n \rightarrow \pi^*$ transitions will be active in this region (at ~260 nm),[22] but may be expected to overlap more with the weaker L_b CD. In addition, it is weaker than the pyridyl $n \rightarrow \pi^*$ CD (for reasons we justify later) and thus unlikely to affect the interpretation of our chosen probes.

Theoretical CD of Pyridyl Crowns. Having defined our interpretative model, we now analyze the theoretical CD for each of the two probe transitions due to the defined dominant perturbers in some detail, thereby predicting the sign and magnitude of the CD expected as a function of the orientations of these perturbers in the crown. The comparison with experimental studies is addressed separately in the section that follows, in order to demonstrate clearly that the theoretical results are obtained without any recourse to empirical CD data.

A. The L_a Transition CD. The close energetic proximity and strong electric dipole character of the amide carbonyl $\pi \rightarrow \pi^*$ and L_a transitions, the spatial proximity of the respective chromophores, and their skewed relative orientations lead to ideal conditions for a strong coupled-oscillator CD at both transitions. As the energy gap is small, an approximate "excitonic" bisignate band (characteristic of degenerate skewed chromophores) may be expected, of which we need only consider the component at the accessible L_a transition energy, the other being of opposite sign and appearing at even higher energy.

For the L_a transition, the origin of the pyridine chromophore may be selected to coincide with that of the ring, the excitation having its parentage in a benzene transition involving the entire π system. The *co* CD for this transition may be written, from eq 20, in the convenient form

$$R_\alpha = K(\mu_\alpha{}^A)^2 t_{\alpha\alpha}{}^C \qquad (27)$$

where K is a *positive* quantity that is fully defined from a comparison of eq 27 and 20 and is constant for the amide carbonyl perturber, absorbing the energy terms (which are particularly large because of the proximity of the two transitions) $(\mu^C)^2$ and the r^{-2} factors. Noting that $\alpha = z'$, and that the terms in X may be neglected as the origin of the amide carbonyl lies relatively close to the $X = 0$ plane (we may, in fact, conveniently assume that the carbonyl transition moment has its origin at the carbonyl carbon), the $t_{z'z'}{}^C$ factor takes the simple form

$$t_{z'z'}{}^C(X = 0) = x'z'[Y - 3Z^2Y] + x'y'[-3ZY^2] \qquad (28)$$

Of the amide carbonyls, only the $Y > 0$ perturber need be considered. For the combined effect of two perturbers related by a C_2 of the crown along the z' direction, the above result is simply doubled. For the case where this symmetry relation does not exist between two perturbers, the CD for the left perturber is identical with that of the system obtained on the right (to which the above expressions apply) by a pure C_2 rotation about the z axis. The positional sector function of $t_{z'z'}(X=0)$ for the first contribution is noded at the position of the carbonyl origin and, for the second contribution, corresponds almost exactly to the

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[22] Schipper, P. E.; Rodger, A. *Spectrochim. Acta* **1988**, *44A*, 575.

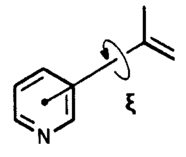

Figure 7. Definition of the ξ angle (see text).

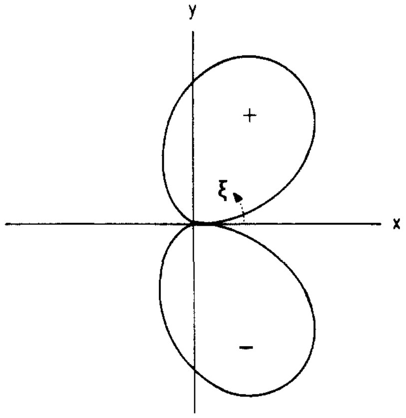

Figure 8. Plot of the orientational sector function as a function of ξ.

critical maximum of the relevant positional sector function. It follows that only the term in $x'y'$ need be considered. The corresponding orientational sector function $x'y'$ may be further expressed in terms of the angle ξ (see Figure 7), defined as the angle of rotation of the carbonyl bond about the bond linking the carbonyl carbon to the pyridine (anticlockwise, looking from the pyridine, and zero for the in-pyridine-plane geometry). The orientational sector function $x'y'$ reduces to the form

$$x'y' = (3/8)\sin\xi(1 + \cos\xi) \tag{29}$$

This is plotted in Figure 8. Thus

$$\mathrm{R}_z(co) = -(0.457)K(\mu_z^{\mathrm{A}})^2 \sin\xi(1 + \cos\xi) \tag{30}$$

i.e., collapses to a simple function of ξ. For the reference perturber with $y' > 0$, the CD is zero when $\xi = 0$, becomes increasingly negative as ξ approaches its maximum negative value at ~60°, and then goes back to zero at 180°. Beyond this point, the mirror image behavior is seen, with a slowly increasing positive CD maximizing at ~300°, and vanishing again at 360° = 0°.

It is important to appreciate that *all* quantities in eq 30 are fully defined in terms of fundamental constants and quantities that can be determined from electronic calculations on the isolated A and C moities (or alternatively, determined experimentally from the normal absorption spectrum of the isolated moities), so that there is absolutely no reference to any empirical CD data. *It therefore represents an analytical expression for the CD for the L_a transition as a function of the structural variable ξ for the defined interpretative model, i.e., the CD spectrum–structure relationship for the L_a transition of the pyridyl crowns in question.* This expression will therefore form the basis for the interpretation of the $\mathrm{L_a}$-transition CD in the section on the comparison with experimental data. Before turning to such comparisons, however, we must effect a parallel analysis for the n-transition CD.

B. The n-Transition CD. The *dc* CD for a magnetically *y*-polarized transition of A may be written in the concise form

$$\mathrm{R}_y(dc) = K_\mathrm{c}\,\mathrm{Im}\{m_y^{\mathrm{A}}\mu_x^{\mathrm{A}}\}[XY]r^{-3} \tag{31}$$

where K_c is a *positive* scalar (proportional to the isotropic polarizability of the perturbing group) and fully defined through a comparison of eq 12 and 31. It follows that perturbers lying near to $X = 0$ may, to a first approximation, be neglected in determining the *dc* CD. In fact, the largest values of the positional sector functions will be expected for "classical" R perturbers, which will act through their isotropic polarizability, and any occupants of the crown holes. In order to determine the full CD behavior, however, it is necessary to determine the A factor, or otherwise there will be an ambiguity in the absolute sign of the overall CD. This may be effected in the following way.

The A factor is a function of the transition density associated with the n → π* transition, which, because of the localized nature of the n orbital, will be predominantly localized on the nitrogen center. A reliable estimate of the A factor may therefore be obtained with a relatively simple description of these orbitals, and a choice of the n-transition origin on the pyridyl nitrogen center. If the lobal signs of the basis p atomic orbital functions are taken to be positive in the positive directions of the (xyz) axes, and that of the s function is positive, then the n state may be written in the form

$$\varphi_n = -c_\mathrm{s}|\mathrm{s}\rangle + c_z|\mathrm{p}_z\rangle \quad (c_\mathrm{s},c_\mathrm{z} > 0) \tag{32}$$

and the π^* state in Hückel form in terms of a p_x basis $\{\varphi_\mathrm{i}\}$, where $i = \mathrm{I}, ..., 6$ around the pyridine ring and $i = 1 = N$; viz.

$$\varphi_{\pi^*} = c(|\varphi_1\rangle + |\varphi_4\rangle) - c'(|\varphi_2\rangle + |\varphi_3\rangle + |\varphi_5\rangle + |\varphi_6\rangle)\ (\mathrm{c,c'} > 0) \tag{33}$$

Using the definition of the magnetic moment operator (eq 8), it follows directly from the properties of p orbitals that (ijk = permutation of Cartesian indexes xyz)

$$\langle \mathrm{p}_i|m_j|\mathrm{p}_k\rangle = (e/2m_\mathrm{e})i\hbar\epsilon_{ijk}(\epsilon_{ijk} = 1,\ ijk \text{ cyclic}, = -1, \text{ acyclic}) \tag{34}$$

Similarly, from the definition of the electric moment operator (eq 9), it follows that

$$\langle\varphi_n|\mu_x|\varphi_{\pi^*}\rangle \simeq -c_\mathrm{s}ce\mu^\circ; \qquad \mu^\circ = \langle \mathrm{s}|x|\varphi_1\rangle > 0 \tag{35}$$

Thus

$$\mathrm{R}_y(dc) = -K_\mathrm{c}\{c_z c_\mathrm{s} c^2\hbar e^2\mu^\circ/2m_\mathrm{e}\}[XY]r^{-3} \tag{36}$$

Equation 36 represents the maximal simplification for the CD of the n transition and is, like eq 30 for the $\mathrm{L_a}$ transition CD, fully defined in terms of fundamental constants and quantities that can be determined from electronic calculations on the isolated A and C moities with absolutely no reference to any empirical CD data. *It therefore represents an analytic expression for the CD for the n transition as a function of the structural coordinates (XYZ), r, and perturber polarizabilities for the defined interpretative model, i.e., the CD spectrum–structure relationship for the n transition of the pyridyl crowns in question.* A summation over the totality of individual perturbers is, as mentioned earlier, implicit.

The above expression confirms pure quadrant behavior and also yields an *absolute* sign allocation of the quadrants, the CD for a perturber in the positive XY quadrant being negative for the AC system. As discussed in the earlier theoretical analysis, if the chromophore is inverted to the A* system, the absolute sign of the n transition for the same crown should change; i.e., the effective quadrant behavior is also inverted. However, there is a codicil to this argument in that the n → π* origin, being situated on the pyridyl nitrogen, will now have a different relative disposition to the set of crown perturbers, and there is also no guarantee that the overall crown conformation of the initial AC system will be retained in the inverted system.

It is instructive to perform a comparable analysis for the n → π* CD of the carbonyl chromophore, for which the absolute sign of the "ideal" octant behavior is well established empirically, and also from detailed calculations. This serves both as a check on the procedure above for the pyridine n → π* CD calculation, as well as providing an estimate of the potential "background" carbonyl CD in the bulk crown. For a z magnetically polarized transition, with $K'_\mathrm{c} > 0$, the *dc* CD may be written in the simplified form

$$R_z(dc) = K'_\mathrm{c}\,\mathrm{Im}\{m_z^{\mathrm{A}}Q_{xy}^{\mathrm{A}}\}[XYZ]r^{-4} \tag{37}$$

where the A factor may be estimated from the approximate state functions (p_y on O, p_x on O, p' on C, lobe conventions as before)

$$|n\rangle \simeq p_y; \qquad |\pi^*\rangle \simeq c_x p_x - c'p' \; (c_x, c' > 0) \tag{38}$$

Writing

$$Q^\circ = \langle p_x|Q_{xy}|p_y\rangle \tag{39}$$

it follows that

$$R_z(dc) = -K_c(\hbar e^2 c_x^2 Q^\circ / 2m_e)[XYZ]r^{-4} \tag{40}$$

This represents the CD spectrum–structure relationship for the CD of the n → π transition of a carbonyl group of assumed C_{2v} symmetry.* It yields the correct octant behavior, both in functional form and absolute sign of the octants. It also demonstrates that the background carbonyl n → π* CD may be expected to be markedly weaker than that of the pyridyl n transition; this follows from noting that the s and p overlap regions lead to higher densities than the p_x, p_y overlap, and thus the pyridine μ° moment will have a more significant effect than the carbonyl Q° moment in leading to CD. In addition, the transition energy at which this background CD appears [it has been suggested that amide and acidic carbonyls have their n → π* transitions at ~260 nm (in alcohols)[22]] coincides more with that of the L_b band, and thus the carbonyl CD is unlikely to effect the analysis of the selected probe transitions.

Comparisons with Experimental Data

All the crowns **1**–**5** have strong CD bands at the L_a and n transitions (see Figures 5 and 6). In all cases, the L_a band is negative in sign, and its sharp slope at higher energy is consistent with the appearance of a "partner" exciton band corresponding to the amide carbonyl. This is fully consistent with the theoretical prediction of the previous section (see eq 30 for the relevant CD spectrum–structure relationship) that the L_a CD will be strongly negative for the experimentally determined basis structure in which the amide carbonyl is found to have (for the reference to the right) $\xi = 30°$, with the other being related by the C_2 axis of the pyridyl and thus contributing constructively.

In addition, all the crowns have an n band that is negative. Noting that all spectra are determined in alcohol, a highly polarizable solvent, this is consistent with the theoretical predictions assuming a dominant contribution from the crown holes (filled with solvent), which lie exclusively in the quadrants that contribute a negative CD (see eq 36 for the relevant CD spectrum–structure relationship). In a sense, the R groups in this case serve to exclude potentially cancelling positive contributions from the solvent if the system was achiral, and thus the CD should increase as the size of the R group increases. This general behavior is found experimentally for the series **1**–**3**.

The exceptional case here is the inverted crown **4**, which should have, if it has a structure similar to the basis structure, a positive n CD and a negative L_a CD. Experimentally, both bands are negative. However, the conformation of the basis structure is partially controlled by H–H repulsions between the amide hydrogens and the CH of the pyridyl group in the AC system, whereas the inverted system presents the pyridyl lone pairs and leads to the potential formation of hydrogen bonds with the amide hydrogens. In such a case, the GSR/ISP expressions for the n-transition CD must be augmented by overlap-dependent dative terms.[23] A preliminary analysis of such additive dative terms suggests a strong negative dative CD contribution for the basis structure geometry, thereby leading to the overall negative n CD for the inverted crown **4**, as observed experimentally. A detailed discussion of this dative mechanism will be published elsewhere. Supporting evidence that such an extra mechanism occurs for the particular crown **4** is supported by the inverted crowns studied by Dyer et al.,[2] for which dativity (hydrogen bonding) is absent. If we assume that their structures are consistent with that of the basis structure, the theoretical expectation of a positive n band and negative L_a band for the inverted complexes is confirmed.

Conclusions

The present analysis for the pyridine crowns suggests that the CD of the pyridine n transition is, in these compounds, a sensitive extrinsic probe of the crown holes, and thus of the nature of the chemical moities present therein. This is a particularly encouraging result as it is, after all, precisely such intercalation processes that are crucial to the practical importance of such crown systems. The CD of the L_a transition, on the other hand, serves as an intrinsic structural probe of the crown backbone. Thus, pyridine is a particularly suitable probe in that it is capable of monitoring, through its two distinct probe transitions, two different aspects of the crown structure.

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Vibrational Optical Activity in *trans*-2,3-Dimethyloxirane

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Abstract: Vibrational circular dichroism (VCD) and Raman optical activity (ROA) spectra for *trans*-2,3-dimethyloxirane are presented. Ab initio vibrational properties obtained with the 6-31G, 6-311G, and 6-31G** basis sets are used to understand the nature of vibrations responsible for the observed bands. On the basis of these vibrational assignments VCD spectral features were interpreted by using the VCD expressions derived for A_2B_2 molecules of C_2 symmetry. The absolute configuration deduced from these VCD interpretations matches that known from other experiments. Recent instrumental developments permitted the measurements of the first ROA spectra in backward scattering for *trans*-2,3-dimethyloxirane. These experimental ROA spectra were analyzed by using the ab initio ROA predictions obtained with the 6-31G and 6-31G** basis sets. For the majority of vibrational bands the predicted ROA signs are in agreement with the observed ones. However, the predicted ROA magnitudes, normalized with the Raman intensities, are usually larger than the experimental magnitudes.

I. Introduction

Vibrational Raman optical activity[1] (ROA) and circular dichroism[2] (VCD) are two new branches of molecular spectroscopy that probe the optical activity associated with vibrational transitions. The major anticipation of vibrational optical activity (VOA) is to provide new approaches for determining the three-

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