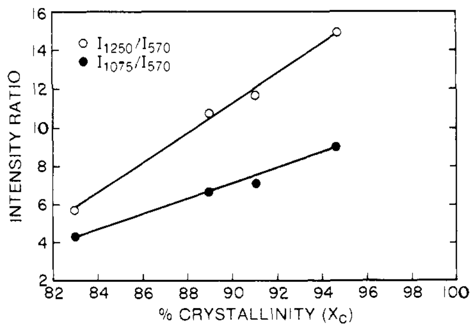

Figure 8. Plot of FTIR relative intensity ratios of vs. degree of crystallinity for etched single-crystal mats (I).

HF solution etching where the rate derived from SAXS analysis was 0.01 Å/min, an order of magnitude lower.[17] The FTIR data in Figure 5 also show linearity when plotted vs. $t^{1/2}$. A combination of data from Figures 5 and 7 is shown in Figure 8, where a linear relationship is derived by plotting FTIR intenstiy ratios vs. crystallinity directly for the etching process on the single crystals.

Examination of the ESCA data serves as another illustration of the difference in sampling depths from FTIR. The etching experiment on the crystal yields ESCA data which plateau before 30 min of etching. This is indicative of both the relatively low level of disordered material in the crystal, which is etched away, and the shallow sampling depth of the technique combining to show a steady state after 15 min of etching. In contrast, ESCA results from the melt cast mats in Figure 6 show continuous linear increases because of the higher concentration of amorphous material in sample II. Both spectroscopic methods thus show changes in relative intensity as crystallinity increases during the chemical etching process. The etching process appears to be very fast for the amorphous material and slower for the crystalline core. Additionally, the complementary use of FTIR and ESCA proved to be very important in deducing the mechanism of the reaction. FTIR evidence showed the growth of Si–OH directly, not easily detectable by ESCA which cannot detect hydrogen.[12,13] ESCA monitored the growth of fluorine, which was not detected by FTIR since bands due to Si–F were masked by the Si–O bands. These data thus provide an extensive chemical and morphological basis for resistance to chemical attack as related to the crystalline structure of this unique material. Work is currently underway, including surface spectroscopic studies by ESCA and SIMS,[14] to further investigate the chemical and morphological basis for differences between crystalline and amorphous regions of polymer systems, which have such an important influence on structure property relationships.

Conclusions

This study has demonstrated a novel use of ESCA to measure differences in surface morphology of a poly(TMpS) homopolymer, manifest throught the use of selective chemical degradation. ESCA and FTIR have been used together successfully to analytically monitor and characterize the changing surface of etched poly(TMpS). These spectroscopic techniques can be employed to monitor the surface chemistry in a way that parallels the crystallinity changes (increase) assessed by DSC and by SAXS measurements. Etching with HF gas, using He diluent, removes the more vulnerable surface material in poly(TMpS) lamellar crystals. In spherulitic specimens the interlamellar regions are more susceptible to chemical attack, degradation also occurring via Si–O–Si chain scission.

Acknowledgment. We acknowledge partial support of this project by the National Science Foundation Polymer (DMR 8113089) and Chemical Analysis (CHE 8108495) Programs.

Registry No. Poly(TMpS), 54811-84-6.

Symmetry Rules for the Determination of the Intercalation Geometry of Host/Guest Systems Using Circular Dichroism: A Symmetry-Adapted Coupled-Oscillator Model

Pieter E. Schipper* and Alison Rodger*

Contribution from the Department of Theoretical Chemistry, The University of Sydney, New South Wales 2006, Australia. *Received June 7, 1982*

Abstract: The intercalation of an achiral guest molecule into a relatively complex chiral host system (e.g., DNA, cyclodextrins) leads to an induced circular dichroism (ICD) of the guest transitions. By exploiting the recently developed generalized selection rules, it is shown that the coupled-oscillator expressions for the guest ICD may be analytically symmetry-adapted for all combinations of host/guest symmetries, leading to a rigorous simplification of the expressions and, more importantly, well-defined conditions under which simple correlations exist relating the ICD sign directly to the intercalation geometry. The results are applied to aromatic guests intercalated into DNA and cyclodextrin hosts, as well as to charge-transfer transitions in chiral metal chelate complexes. Good agreement with experimental results is obtained.

Introduction

The intercalation of aromatic chromophores (guest species) into DNA and cyclic sugars (host species) in aqueous media has been the subject of extensive experimental investigation because of the potential role of intercalation in biological phenomena such as mutagenicity and carcinogenicity.[1-7] Determination of the intercalation geometry by standard X-ray diffraction or NMR methods is virtually precluded by the low concentrations of the intercalated species and the need to study the systems in solution. Such conditions are, however, ideally suited to absorption spectroscopic methods. Linear dichroism (LD) has been used ex-

---

(1) Kamiya, M. *Biochim. Biophys. Acta* **1979**, *562*, 70, and references therein. (Note that the considerations of this paper are restricted to low adduct concentrations in the DNA case and do not apply to the high concentration limit in which chiral superstructure of the dye are formed.)

(2) Schipper, P. E.; Nordēn, B.; Tjerneld, F. *Chem. Phys. Lett.* **1980**, *70*, 17.

(3) Harata, K.; Uedaira, H. *J. Chem. Soc. Jpn.* **1975**, *48*, 375.

(4) Nordēn, B. *Appl. Spectrosc. Rev.* **1978**, *14*, 157.

(5) Shimuzu, H.; Kaito, A.; Hatano, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2678; **1981**, *54*, 513.

(6) Yamaguchi, H.; Ikeda, N.; Hirayama, F.; Uekama, K. *Chem. Phys. Lett.* **1978**, *55*, 75.

(7) Ikeda, N.; Yamaguchi, H. *Chem. Phys. Lett.* **1978**, *56*, 167.

0002-7863/83/1505-4541$01.50/0

tensively by Nordên and co-workers for dye–DNA systems to determine intercalation geometry with respect to the DNA major axis. More recently,[2] it was suggested that the orientation with respect to axes fixed in the plane of the DNA bases could be determined through the measurement of the induced circular dichroism (ICD) of the guest transitions. It is with the latter, and its generalization to a range of host–guest systems, that this paper will be exclusively concerned.

We consider an achiral guest and a chiral host. The ICD of the guest transitions will then be directly the result of the guest–host coupling and hence of their relative orientations. If only the electric dipole allowed transitions of the guest are considered, the guest ICD may be discussed theoretically in terms of the coupled-oscillator model as developed by Kirkwood,[8] Kuhn,[9] and Moffitt;[10] the ICD arises in this case through a nondegenerate dipolar coupling of the host and guest transitions. An introduction to this model and the resultant symmetry properties for a two-oscillator system appears in the review by Schellman.[11] Extension to higher multipolar terms has been considered by Tinoco[12] for degenerate chromophores, but for nondegenerate chromophores of the type discussed in this paper, the rapid radial convergence of the chromophore–chromophore coupling ensures dominance of the purely dipolar terms. The most important feature of the coupled-oscillator model is the simple fact that it works, quantitatively as well as qualitatively, in accounting for the measured ICD for electric dipole allowed guest transitions.

There are difficulties in applying the model to more complex host–guest systems in which the host cannot be represented as a single chromophoric system. In such cases, the representation of the host as a multichromophoric system leads to contributions to the guest ICD from each guest–host chromophore combination, so that the symmetry rules for each individual coupling are lost. The interesting feature that has emerged from recent studies attacking the problem in this way is that frequently, despite the relative complexity of the host systems, simple correlations in the sign of the ICD bands and the intercalation geometry result from detailed calculations. The first systematic attempt at a determination of the source of such seemingly fortuitous correlations was that directed at dye/DNA systems in which the sign/geometry correlations emerged naturally from the coupled-oscillator model if certain physical assumptions were valid.[2]

In this paper, we attack the problem of ICD sign/geometry correlations and the reduction of the ICD expressions to their simplest form at the most fundamental level, and show that they result from underlying symmetries of the host, the guest, and the intercalation geometry. For example, the host system, being chiral, can be of C_n or D_n symmetry (e.g., the cyclodextrins have C_6, C_7, C_8 symmetries), and the guest is taken to be achiral and thus will be of relatively high symmetry (e.g., C_{2v}, D_{2h} for many aromatic guests). In addition, the nature of the intercalation modes are usually restricted by physical factors to those satisfying certain symmetry requirements (e.g., intercalation into cyclodextrins require the guest to come along the major symmetry axis of the host). By incorporating such symmetries analytically into the ICD expressions, the conditions when simple sign/geometry correlations are expected may be derived. Furthermore, in systems without an obvious C_n symmetry (the existence of a host C_n axis is the factor responsible for the simplification of the host properties), the empirical observation of sign correlations implies an underlying pseudosymmetry of the host which may be interpreted directly to give information about the host structure and the intercalation geometry. This is so for DNA hosts, as we shall see later. In fact, the physical assumptions in the recent dye/DNA paper[2] are shown here to be a particular case of a set of conditions for the existence of a pseudo-C_2 axis in DNA.

The importance of host and guest symmetry in reducing the guest ICD to a simple form was first illustrated in a paper on a seemingly unrelated problem of charge-transfer CD in tris(bidentate) complexes.[13] The charge-transfer (CT) chromophore may be identified as the guest, with the chelates constituting a multichromophoric host. By the use of the generalized selection rules,[14] the guest ICD is analytically reduced to the simplest expression under the guest symmetry (taken to be D_{3d}); finally, because of the D_3 host symmetry, it is shown that the ICD of the guest CT transitions may be simply expressed in terms of the chelate exciton CD, and that the polarizations of the CT transitions (the geometry in this instance being well defined) may be determined directly through the sign of the ICD. Unfortunately, an error of sign in this earlier paper leads to erroneous conclusions which will be rectified in a later section.

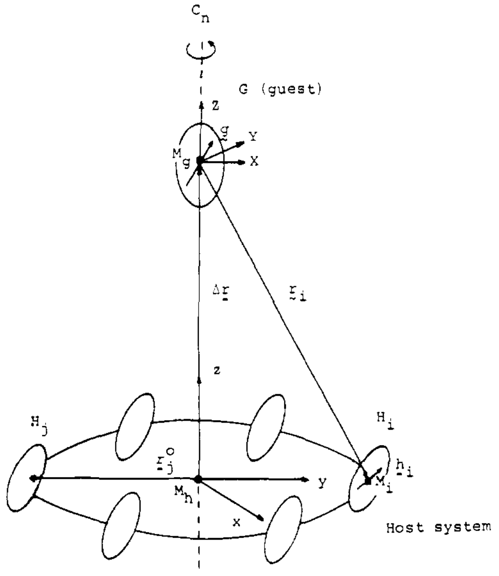

Figure 1. Coordinate systems (*XYZ*: guest-fixed; *xyz*: host-fixed) for a guest intercalating along the C_n host axis. M_h is the symmetry origin of the host, M_g that of the guest.

In this paper, this procedure is generalized to guest–host systems of all possible symmetries. The ICD expressions are firstly written as a scalar product of separate guest and host tensors. The guest tensor is then simplified using the generalized selection rules under the guest symmetry. The host tensor is analogously simplified using the host symmetry. Finally, the conditions under which simple sign correlations exist are determined through examination of possible guest/host symmetry combinations and symmetry aspects of the intercalation process. At all stages in the procedure, the quantitative rigor of the model is retained, the symmetry reductions being effected analytically on the general coupled-oscillator expressions. The importance of such analytic reductions is that they concomitantly elicit the conditions under which the final ICD rigorously decouples into separate host and guest scalars, a prerequisite for parametrization of the host factor. In fact, such decoupling allows for empirical determination of the host factor, which is of practical importance for relatively complex hosts for which ab initio determination of the host factor is impractical; furthermore, the conditions for sign correlations and simple host parametrization are inextricably connected.

Finally, the results are applied to three particular cases: the intercalation of substituted benzenes into cyclodextrins; the geometry of dye/DNA systems; and the ICD of CT chromophores in tris(bidentate) metal complexes. Good agreement with experimental results is obtained.

The Coupled-Oscillator Model

Consider a guest molecule G with an electric dipole allowed transition of electric dipole transition moment g and transition energy ϵ_g, with a guest-fixed axis system (*XYZ*) at the guest origin M_g as illustrated in Figure 1. The host is taken to have a major

---

(8) Kirkwood, J. G. *J. Chem. Phys.* **1937**, *5*, 479.
(9) Kuhn, W. *Trans. Faraday Soc.* **1930**, *26*, 293.
(10) Moffitt, W. *J. Chem. Phys.* **1956**, *25*, 467.
(11) Schellman, J. *Acc. Chem. Res.* **1968**, *1*, 144.
(12) Tinoco, I., Jr. *Int. J. Quantum Chem.* **1979**, *16*, 111.
(13) Schipper, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 6826.
(14) Schipper, P. E. *J. Am. Chem. Soc.* **1978**, *100*, 3658.

rotational symmetry axis C_n along the z axis of the host-fixed axis system (xyz) centered on the origin M_h. The host is partitioned into n identical chromophores H_i ($i = 1, \ldots, n$), each with a single excited state with electric dipole transition moment $\mathbf{h}_i$ and transition energy ϵ_h. (The restriction to a single host excited state is simply a notational convenience and will be relaxed later.) This partitioning is frequently physically realistic (e.g., in tris(bidentates), the H_i are the separate chelates, whereas in DNA, they are the separate base pairs), but for less obvious systems such as the cyclodextrins, it may be justified by empirical validation of the model.

The guest transition attains its CD activity through nondegenerate coupling with each host chromophore transition separately. The overall guest ICD then has the form

$$R_g = -\frac{1}{\hbar}\sum_{i=1}^{n}\frac{\epsilon_h\epsilon_g}{r_i^3(\epsilon_h^2 - \epsilon_g^2)}(\mathbf{g}\cdot\mathbf{h}_i - 3\mathbf{g}\cdot\hat{\mathbf{r}}_i\mathbf{h}_i\cdot\hat{\mathbf{r}}_i)\ (\mathbf{h}_i\cdot\mathbf{g} \times \mathbf{r}_i) \quad (1)$$

where $\mathbf{r}_i$ is the vector from the guest origin M_g to that of the host chromophore M_i, with the cap denoting the unit vector and $r_i = |\mathbf{r}_i|$. The guest and host terms may be formally separated by rewriting the above in tensor notation as

$$R_g = -\frac{1}{\hbar}\frac{\epsilon_h\epsilon_g}{(\epsilon_h^2 - \epsilon_g^2)}\tilde{T}_g{:}\sum_i \tilde{T}_i/r_i^3 \quad (2)$$

where $\tilde{A}{:}\tilde{B} = \sum_{\alpha\beta}A_{\alpha\beta}B_{\alpha\beta}$ and α, β run over x, y, z. The tensors $\tilde{T}_g$, $\tilde{T}_i$ are defined as

$$\tilde{T}_g = \mathbf{gg} \quad (3)$$

and

$$\tilde{T}_i = \tilde{T}_i^{(0)} + \tilde{T}_i^{(1)} + \tilde{T}_i^{(2)} \quad (4)$$

with

$$\tilde{T}_i^{(0)} = \mathbf{h}_i[\mathbf{r}_i^0 \times h_i] \quad (5)$$

$$\tilde{T}_i^{(1)} = \mathbf{h}_i[\Delta\mathbf{r} \times \mathbf{h}_i] \quad (6)$$

$$\tilde{T}_i^{(2)} = -3(\mathbf{h}_i\cdot\mathbf{r}_i)\hat{\mathbf{r}}_i[\hat{\mathbf{r}}_i \times \mathbf{h}_i] \quad (7)$$

The partitioning of the host tensor into three contributions $\tilde{T}_i^{(\nu)}$ will be shown to have a physical origin in terms of full and partial intercalation, and follows from noting that, as shown in Figure 1,

$$\mathbf{r}_i = \mathbf{r}_i^0 + \Delta\mathbf{r} \quad (8)$$

where $\Delta\mathbf{r}$ is the vector from the guest origin M_g to the overall host origin M_h, and $\mathbf{r}_i^0$ the vector from the overall host origin M_h to the origin M_i of the host chromophore H_i. (M_h lies in the plane of the M_i origins.)

An important feature of the host tensor $\tilde{T}_i$, even in this general form, is that each contribution is individually traceless, so that the host tensor

$$\tilde{T}_h = \sum_i \tilde{T}_i/r_i$$

is also traceless. This property of the host tensor, coupled with the symmetry arguments that follow, is ultimately responsible for the sign correlations. To see this more clearly, we now turn to the systematic incorporation of host and guest symmetries.

Incorporation of Host and Guest Symmetries

The guest and host tensors can now be separately simplified for their respective symmetries. Although the tensors of eq 2 are expressed in terms of a common host (xyz) system, we shall first consider the simplification of the guest tensor in the guest system (XYZ), and of the host tensor in the host system (xyz). We then discuss the relations between these two axis systems.

The Guest Tensor. The guest tensor in terms of the guest system (XYZ) has the general form

$$\tilde{T}_g = \mathbf{gg} = \begin{bmatrix} g_Xg_X & g_Xg_Y & g_Xg_Z \\ g_Yg_X & g_Yg_Y & g_Yg_Z \\ g_Zg_X & g_Zg_Y & g_Zg_Z \end{bmatrix} \quad (9)$$

Simplification of the tensor proceeds through the generalized selection rules,[14] a two-stage procedure in which operator products are first simplified through the operator selection rules (OSR), and then the effects of state symmetries are incorporated through the state selection rules (SSR). If the guest has symmetry K_g with N operations R_ξ ($\xi = 1, 9\ .\ ., N$), then the OSR dictate that the guest tensor has the form

$$\tilde{T}_g = \mathcal{P}^0\mathbf{gg} \quad (10)$$

where

$$\mathcal{P}^0 = \frac{1}{N}\sum_{\xi=1}^{N} R_\xi \quad (11)$$

$\mathcal{P}^0$ is the totally symmetric projection operator of the group K_g. Only five forms of the guest tensor are possible, and may be directly related to the degeneracy of the point group. Only achiral point groups need be considered, it being assumed that the isolated guest is CD inactive.

Triply Degenerate Groups: T_d, O_h. In the triply degenerate groups, the (XYZ) axes are formally indistinguishable, and the guest tensor under the OSR has the form

$$\tilde{T}_g = {}^1/_3(g_Xg_X + g_Yg_Y + g_Zg_Z)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (12)$$

The state selection rules simply dictate that the prefactor (the total dipole strength) is nonzero only for triply degenerate T_u transitions.

Doubly Degenerate Groups: C_{nv}, C_{nh}, D_{nh} ($n > 2$); S_{2n}, D_{nd}. In the doubly degenerate groups, there exists a unique C_n axis (the Z direction), but the X and Y directions are formally indistinguishable, leading to a possible double degeneracy. The guest tensor under the OSR has the form

$$\tilde{T}_g = \begin{bmatrix} {}^1/_2(g_Xg_X + g_Yg_Y) & 0 & 0 \\ 0 & {}^1/_2(g_Xg_X + g_Yg_Y) & 0 \\ 0 & 0 & g_Zg_Z \end{bmatrix} \quad (13)$$

Application of the state selection rules partitions the above into two separate tensors, one for the singly degenerate Z-polarized transitions of A symmetry ($\tilde{T}_g$(A)), and one for the doubly degenerate XY-polarized transitions of E symmetry ($\tilde{T}_g$(E)). For an A transition,

$$\tilde{T}_g(\mathrm{A}) = g_Zg_Z\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (14)$$

whereas for an E transition,

$$\tilde{T}_g(\mathrm{E}) = {}^1/_2(g_Xg_X + g_Yg_Y)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (15)$$

Singly Degenerate Groups with XZ, YZ Reflections: C_{2v}, D_{2h}. In the singly degenerate groups with XZ, YZ reflections, the X, Y, Z axes are all formally distinguishable, so that no degeneracy is possible. Application of the OSR leads to the form

$$\tilde{T}_g = \begin{bmatrix} g_Xg_X & 0 & 0 \\ 0 & g_Yg_Y & 0 \\ 0 & 0 & g_Zg_Z \end{bmatrix} \quad (16)$$

The SSR lead to three separate tensors corresponding to the three types of electric dipole allowed transitions under these symmetries: X-polarized, Y-polarized, and Z-polarized with respective symmetries B_1, B_2, A_1 in C_{2v}, and B_{1u}, B_{2u}, B_{3u} in D_{2h}. The three state selected tensors are simply partitioned tensors arising from eq 16, having the form

$$\tilde{T}_g(B_1, B_{1u}) = g_Xg_X\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (17)$$

$$\tilde{T}_g(B_2, B_{2u}) = g_Yg_Y\begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (18)$$

$$\tilde{T}_g(A_1, B_{3u}) = g_Zg_Z\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (19)$$

Single Degenerate Groups with Only XY Reflection: C_{1h}, C_{2h}. For these groups, the OSR lead to the guest tensor

$$\tilde{T}_g = \begin{bmatrix} g_X g_X & g_X g_Y & 0 \\ g_Y g_X & g_Y g_Y & 0 \\ 0 & 0 & g_Z g_Z \end{bmatrix} \tag{20}$$

In this case, the guest tensor is no longer diagonal, because the X, Y axes are formally inequivalent (nondegenerate), but not uniquely determined by symmetry. Only the Z axis is unique. The SSR lead to two possible types of electric dipole allowed transitions: Z-polarized (A″, A_u symmetry) and XY-polarized (A′, B_u symmetry in C_{1h} C_{2h}, respectively). The corresponding tensors have the form

$$\tilde{T}_g(A'',A_u) = g_Z g_Z \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{21}$$

$$\tilde{T}_g(A',B_u) = \begin{bmatrix} g_X g_X & g_X g_Y & 0 \\ g_Y g_X & g_Y g_Y & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{22}$$

Singly Degenerate Group with Inversion Only: C_i. For C_i, the guest tensor retains the full form of eq 9, under both the OSR and the SSR, there being only one type of electric dipole allowed transition of A_u symmetry. None of X, Y, Z are formally distinguishable, nor are they in any way symmetry determined.

The Host Tensor. Full exploitation of the host symmetry requires a restriction on the mode of intercalation: viz., that the guest origin lies on the major C_n axis of the host. This direction usually corresponds to the only physically realistic direction for intercalation to occur, so that the restriction constitutes the first of several conditions which are required in order to get meaningful sign correlations. Noting that in this case $r_i = r$ for all i, eq 2 reduces to the form

$$R_g = -\frac{1}{h}\frac{\epsilon_h \epsilon_g}{r^3(\epsilon_h^2 - \epsilon_g^2)}\tilde{T}_g : \sum_{\nu=0}^{2} \tilde{T}_h^{(\nu)} \tag{23}$$

where $\tilde{T}_h^{(\nu)} = \sum_i \tilde{T}_i^{(\nu)}$ and the $\tilde{T}_i^{(\nu)}$ are defined in eq 5–7.

As the host has a C_n symmetry axis and thus n rotations $\mathscr{C}_n^{\xi}$ ($\xi = 1, \ldots, n$), the tensors $\tilde{T}_i^{(\nu)}$ may be written in terms of those of chromophore 1 as

$$\tilde{T}_i^{(\nu)} = \mathscr{C}_n^{i-1}\tilde{T}_1^{(\nu)} \tag{24}$$

(Note that the operator $\mathscr{C}$ is here used in an abstract sense and is not a matrix.) It follows that

$$\tilde{T}_h^{(\nu)} = \sum_i \mathscr{C}_n^{i-1}\tilde{T}_1^{(\nu)} \tag{25}$$

Each tensor $\tilde{T}_1^{(\nu)}$ has the general form $\mathbf{a}_1^{(\nu)}[\mathbf{b}_1^{(\nu)} \times \mathbf{c}_1^{(\nu)}]$ so that $\tilde{T}_h^{(\nu)}$ may be written directly in terms of the components of the vectors $\mathbf{a}_1^{(\nu)}$, $\mathbf{b}_1^{(\nu)}$, and $\mathbf{c}_1^{(\nu)}$. Leaving the super- and subscripts understood for convenience, $\tilde{T}_h^{(\nu)}$ takes two possible forms, depending on the value of n. For $n = 2$, whereas for $n > 2$,

$$\tilde{T}_h(\nu) = 2\begin{bmatrix} a_x(b_y c_z - b_z c_y) & a_x(b_z c_x - b_x c_z) & 0 \\ a_y(b_y c_z - b_z c_y) & a_y(b_z c_x - b_x c_z) & 0 \\ 0 & 0 & a_z(b_x c_y - b_y c_x) \end{bmatrix} \tag{26}$$

$$\tilde{T}_h^{(\nu)} = n\begin{bmatrix} \begin{matrix} {}^1\!/_2[a_x(b_y c_z - b_z c_y) \\ \quad + a_y(b_z c_x - b_x c_z)] \end{matrix} & \begin{matrix} {}^1\!/_2[a_x(b_z c_x - b_x c_z) \\ \quad - a_y(b_y c_z - b_z c_y)] \end{matrix} & 0 \\ \begin{matrix} -{}^1\!/_2[a_x(b_z c_x - b_x c_z) \\ \quad - a_y(b_y c_z - b_z c_y)] \end{matrix} & \begin{matrix} {}^1\!/_2[a_x(b_y c_z - b_z c_y) \\ \quad + a_y(b_z c_x - b_x c_z)] \end{matrix} & 0 \\ 0 & 0 & a_z(b_x c_y - b_y c_x) \end{bmatrix} \tag{27}$$

The effect of the host symmetry is therefore to reduce the host tensor to a form containing quantities pertaining to only one of the chromophores in the total host system. Although the host tensor is in general nondiagonal, it is still, as mentioned earlier, traceless. The detailed form of each $\tilde{T}_h^{(\nu)}$ will be considered after some discussion of the interaction symmetry, as we shall then see that only the diagonal elements are needed.

Restriction of Intercalation Modes

We can now draw these results together to elicit the conditions under which simple parametrization and sign correlations will occur. Crucial to the existence of the sign correlations is the tracelessness of the host tensor, indicating that mutually cancelling positive and negative elements will generally appear in different positions on the diagonal. The condition under which only the diagonal elements of the host tensor appear in the general expression of eq 23 is simply that where the host or guest tensors are diagonal in the (xyz) system. As the host tensor is generally nondiagonal, this reduces to the condition that the guest tensor is diagonal in (xyz). We have already seen that the guest tensor is diagonal in (XYZ) in all cases except when the guest has C_{1h}, C_{2h}, or C_i symmetry. These guest symmetries will therefore be ignored, for reasons that will be justified presently. For all other guest symmetries, the guest tensor remains diagonal provided the (XYZ) system is a simple permutation of the (xyz) system (i.e., that the unlabeled axis systems of the guest and host may be superposed). For threefold and higher host rotational axes, it is only necessary that one of the symmetry determined guest axes is coincident with the host z axis, as the host xy degeneracy then leaves the choice of x and y free. Defining the vector

$$\mathbf{t}_g = [(T_g)_{xx};(T_g)_{yy};(T_g)_{zz}]$$

(where the $(T_g)_{\alpha\alpha}$ are the diagonal elements of the guest tensor), and using analogous definitions for the vectors $\mathbf{t}_h^{(\nu)}$ in terms of the diagonal elements of the constituent host tensors $\tilde{T}_h^{(\nu)}$, the ICD then reduces to the simpler form

$$R_g = -\frac{1}{h}\frac{\epsilon_g \epsilon_h}{r^3(\epsilon_h^2 - \epsilon_g^2)}\mathbf{t}_g \cdot \sum_{\nu} \mathbf{t}_h^{(\nu)} \tag{28}$$

The permutative relationship between the host/guest axis sytsems has here been introduced as a necessary condition for eq 23 to collapse to the simpler form of eq 28, which we shall see is necessary to obtain simple sign correlations. Fortunately, this relationship will frequently occur in real systems because the individual host/guest symmetries lead to symmetries in the host/guest interactions, and subsequently a natural restriction of stable intercalation modes to those in which some coincidence of the host and guest symmetry-determined axes will occur. For example, a $C_{\infty v}$ molecule would be expected to intercalate either parallel to the C_n host axis, or perpendicular to it; in both cases, the intercalation modes correspond to cases where the host and guest systems are permutatively related.

It now becomes clear why the C_{1h}, C_{2h} and C_i guest symmetries may be ignored. The total lack of the symmetry definition of the X, Y axes also leads to no natural symmetry definition of the intercalation modes, so that, physically, coincidence of the symmetry axes of the host and guest is unlikely. The neglect of these groups is not merely a matter of convenience; it is simply that sign correlations are not expected as there is no unique symmetry definition of the intercalation modes. A similar argument applies to C_2 hosts, for which only the z axis is symmetry defined. Intercalation modes can be uniquely defined for a particular type of C_2 system (see Figure 2), which fortunately turns out to be the type of C_2 system found in DNA. In this case, (i) the host chromophores H_1 and H_2 are planar; (ii) the molecular planes are perpendicular to the vector $\mathbf{r}_1^0$ ($=-\mathbf{r}_2^0$); and (iii) the host transition is polarized in the molecular plane (i.e., $\mathbf{h}_1 \cdot \mathbf{r}_1^0 = 0$). Defining the y axis along r_1^0, restrictions (i) and (ii) are structural factors leading to a unique definition of the y axis. For example, simple aromatics will intercalate with their planes also perpendicular to this direction. The third restriction is a spectroscopic one which ensures that the same unique y axis is defined by the electronic properties of the host. We shall restrict further discussion to C_2 systems of this type.

It is now possible to discuss how the sign correlations arise from eq 28. Consider first a guest of O_h or T_d symmetry. Such sym-

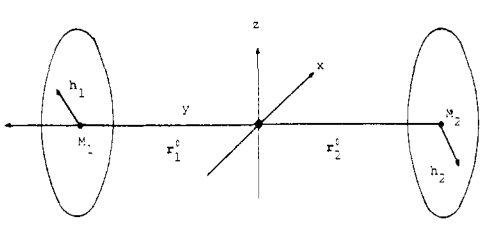

Figure 2. Geometry of C_2 systems for which sign correlations are expected (see text).

metries are (in the dipole approximation) effectively spherically symmetric in that the guest tensor is invariant to the choice of X, Y, Z. Thus the guest tensor is automatically diagonal in the host system, and

$$\mathbf{t}_g = \frac{1}{3}(g_x g_x + g_y g_y + g_z g_z)[1;1;1]$$

Noting that $[1;1;1]\cdot\mathbf{t}_h^{(\nu)} = 0$ because of the tracelessness of each host tensor, it follows that $R_g = 0$. This has a simple physical interpretation in that a spherically symmetric system and a single directed moment at different origins constitute an achiral system (as a mutual reflection plane can always be found). In fact, we may say that the ICD induced in the x, y, z directions exactly cancel. If the degeneracy is lifted in the guest, differently polarized transitions will pick up different diagonal elements of the host tensor, with the result that the sign pattern will mimic those of the host vector $\mathbf{t}_h$. A proper discussion of the sign correlations must, however, be cognizant of the manifold of states on each host chromophore, and will be deferred to the next section.

We have still not explicitly determined the host vectors $\mathbf{t}_h^{(\nu)}$ which will be remedied now. These may be determined directly from eq 5–7 and 26 and 27. It is stressed that all the quantities appearing in the expressions refer to chromophore 1, the subscript being suppressed for convenience. Two physical situations may be distinguished.

Full Intercalation. For full intercalation, $\Delta\mathbf{r} = 0$ and the guest origin is coincident with that of the host M_h. Then $\mathbf{t}_h^{(1)} = \mathbf{t}_h^{(2)} = 0$ and

$$\mathbf{t}_h^{(0)}(n > 2) = (n/2)h_z(h_x r_y^0 - h_y r_x^0)[1;1;-2] \tag{29}$$

$$\mathbf{t}_h^{(0)}(n = 2) = 2h_z h_x r_y^0[1;0;-1] \tag{30}$$

These results follow from expansion of eq 5–7 and substitutions into eq 26 and 27.

Partial Intercalation. Partial intercalation corresponds to $\Delta\mathbf{r} \neq 0$. Then $\mathbf{t}_h^{(1)} = 0$ and $\mathbf{t}_h = \mathbf{t}_h^{(0)} + \mathbf{t}_h^{(2)}$ has the form

$$\mathbf{t}_h(n > 2) = (n/2)h_z(h_x r_y^0 - h_y r_x^0)\{1 - 3(\Delta r/r)^2(1 + \mathbf{h}\cdot\mathbf{r}^0/\mathbf{h}\cdot\Delta\mathrm{r})\}[1;1;-2] \tag{31}$$

$$\mathbf{t}_h(n = 2) = 2h_z h_x r_y^0\{[1;0;-1] - 3(\Delta r/r)^2[0;1;-1]\} \tag{32}$$

We shall discuss the effects of partial intercalation in more detail later; firstly, however, we restrict consideration to the full intercalation case.

Sign Correlations and Parametrization in Fully Intercalated Systems

For fully intercalated systems, eq 28–30 may be combined to give the ICD arising from a single transition moment on each chromophore H_i. Noting that each H_i has a manifold of states and that the ICD has been expressed in terms of the properties of chromophore H_1, then it is necessary to introduce only a sum over states (i.e., over **h**) of this chromophore.

Host Systems with *n* > 2. For $n > 2$, the ICD takes the form

$$R_g = (\epsilon_g/r^3)\mathcal{H}(\epsilon_g)\mathbf{t}_g\cdot[1;1;-2] \tag{33}$$

where

$$\mathcal{H}(\epsilon_g) = \sum_h \frac{n\epsilon_h h_z(h_y r_x^0 - h_x r_y^0)}{2\hbar(\epsilon_h^2 - \epsilon_g^2)} \tag{34}$$

Although $\mathcal{H}(\epsilon_g)$ is strictly a function of ϵ_g, we shall loosely refer to it as the *host parameter*. It becomes a pure host function only in the limit $\epsilon_g \to 0$ (or alternatively, $\epsilon_g \ll \epsilon_h$), for which the host parameter may be written as $\mathcal{H}(0)$. In this limit, for singly degenerate guest systems (C_{2v}, D_{2h}), the *reduced* ICD ($\bar{R}_g(\gamma)$) for a guest transition of γ polarization ($\gamma = x, y, z$) has the form

$$\bar{R}_g(\gamma) = R_g(\gamma)/\epsilon_g^{\gamma} g_\gamma g_\gamma = r^{-3}\mathcal{H}(0)(1 - 3\delta_{\gamma z}) \tag{35}$$

As $\mathcal{H}(0)$ in this limit is strictly a separable, constant host parameter, it follows that

$$\bar{R}_g(x) = \bar{R}_g(y) = -2\bar{R}_g(z) \tag{36}$$

leading to the sign correlations, the sign of $\bar{R}_g(x)$ being that of $\mathcal{H}(0)$.

Equation 35 links three separate factors: (i) the host parameter $\mathcal{H}(0)$; (ii) the polarization of the guest transition Γ ($= X$, Y, or Z); (iii) the intercalation mode (through the coincidence of Γ with host axis γ). The measurement of the reduced ICD allows the determination of any *one* of these if the other two are known. In application to the determination of the intercalation geometries of a range of guests in a particular host, $\mathcal{H}(0)$ may be determined empirically from the reduced ICD of a reference guest for which (ii) and (iii) are known. The intercalation modes of the other guests may then be determined from the measured reduced ICD and factors (i) and (ii). For example, if $\mathcal{H}(0) > 0$, and $\bar{R}_g(\gamma) < 0$ then $\gamma = z$; if the transition at energy ϵ_g^{γ} is Γ-polarized (guest system), then it follows that the intercalation geometry can be specified through coincidence of Γ and the host z axis. Note that, as mentioned earlier, the ICD cannot discriminate between the host x and y axes, consistent with the xy degeneracy of the host.

Staying with the singly degenerate guests for the moment, we now turn to another situation where $\mathcal{H}(\epsilon_g)$ may be reduced to a simpler form. Suppose there exists a low-lying host state such that

$$0 < \Delta\epsilon = \epsilon_h - \epsilon_g \ll \epsilon_h \sim \epsilon_g$$

Then it may be assumed that a single host state dominates. so that

$$\mathcal{H}(\Delta\epsilon) = \frac{n h_z(h_y r_x^0 - h_x r_y^0)}{4\hbar\Delta\epsilon} \tag{37}$$

Although $\mathcal{H}(\Delta\epsilon)$ is a function of ϵ_g through the factor $\Delta\epsilon$, the *sign* will still be constant, so that the procedure of the previous paragraph will still apply.

For the more genneal case, there is no guarantee that $\mathcal{H}(\epsilon_g)$ will have the same sign for all values of $\epsilon_g < \epsilon_h$ (a restriction resulting simply from the fact that experimental measurement of the reduced ICD is only possible in the energy region where the host is strictly CD inactive), as the sign of the numerator will be positive for some host chromophore transitions, negative for others. Thus sign correlations are, strictly speaking, expected only for host/guest systems in which $\mathcal{H}(\epsilon_g)$ reduces to $\mathcal{H}(0)$ or $\mathcal{H}(\Delta\epsilon)$; i.e., when host parametrization is theoretically possible.

Having discussed the nature of host parametrization and its role in leading to sign correlations in a somewhat general way, we now return to the case where the guest is doubly degenerate. Denoting $\bar{R}_g(\gamma\eta)$ as the reduced ICD of a $\gamma\eta$-polarized transition, where

$$\bar{R}_g(\gamma\eta) = \frac{R_g(\gamma\eta)}{\frac{1}{2}\epsilon_g^{\gamma\eta}(g_\gamma g_\gamma + g_\eta g_\eta)} \tag{38}$$

if follows from eq 28–30 and the forms of the guest tensor (eq 13–15) that if the guest degeneracy is (i) in the xy plane,

$$\bar{R}_g(xy) = 2\mathcal{H}(\epsilon_g^{xy})/r^3 \tag{39}$$

$$\bar{R}_g(z) = -2\mathcal{H}(\epsilon_g^{z})/r^3 \tag{40}$$

(ii) in the xz plane (with analogous expressions for the yz plane),

$$\bar{R}_g(xz) = -\mathcal{H}(\epsilon_g^{xz})/r^3 \tag{41}$$

$$\bar{R}_{\mathrm{g}}(y) = \mathcal{H}(\epsilon_{\mathrm{g}}{}^{y})/r^3 \tag{42}$$

The sign correlations for the limiting cases where $\mathcal{H}(\epsilon_{\mathrm{g}})$ reduces to $\mathcal{H}(0)$ or $\mathcal{H}(\Delta\epsilon)$ follow directly from these results. For triply degenerate guests, the ICD vanishes as discussed earlier.

Host Systems with $n = 2$. For the $n = 2$ hosts under the restrictions discussed earlier ($\mathbf{h}_1 \cdot \mathbf{r}_1 = 0$; $\mathbf{r}_1$ defines y axis) and a *singly degenerate* guest, the reduced ICD may be written from eq 28 and 30 in the form

$$\bar{R}(x) = (1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{x}) \tag{43}$$

$$\bar{R}(y) = 0 \tag{44}$$

$$\bar{R}(z) = -(1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{z}) \tag{45}$$

where

$$\mathcal{H}^*(\epsilon_{\mathrm{g}}) = -\sum_h \frac{2\epsilon_h h_z h_x r_y{}^0}{\hbar(\epsilon_{\mathrm{h}}{}^2 - \epsilon_{\mathrm{g}}{}^2)} \tag{46}$$

The ICD discriminates between transition moments aligned along x or z. For *doubly degenerate* guests,

$$\bar{R}_{\mathrm{g}}(xy) = (1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{xy}) \tag{47}$$

$$\bar{R}_{\mathrm{g}}(z) = -(1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{z}) \tag{48}$$

if the degeneracy is in the xy plane;

$$\bar{R}_{\mathrm{g}}(xz) = 0 = \bar{R}_{\mathrm{g}}(y) \tag{49}$$

if the degeneracy is in the xz plane; and finally

$$\bar{R}_{\mathrm{g}}(yz) = -(1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{xy}) \tag{50}$$

$$\bar{R}_{\mathrm{g}}(x) = (1/r^3)\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{x}) \tag{51}$$

if the degeneracy is in the yz plane. The sign correlations in these cases follow directly for the case when $\mathcal{H}^*(\epsilon_{\mathrm{g}})$ reduces to $\mathcal{H}^*(0)$ or $\mathcal{H}^*(\Delta\epsilon)$.

Sign Correlations in Partially Intercalated Systems

The ICD expression for partial intercalation is derived by substitution of eq 31 into eq 28.

Host System with $n > 2$. For xy-degenerate hosts, the ICD may be written in the form

$$\bar{R}_{\mathrm{g}} = (\epsilon_{\mathrm{g}}/r^3)\mathcal{H}_{\mathrm{p}}(\epsilon_{\mathrm{g}})\mathbf{t}_{\mathrm{g}} \cdot [1;1;-2] \tag{52}$$

where

$$\mathcal{H}_{\mathrm{p}}(\epsilon_{\mathrm{g}}) = \sum_h \frac{n\epsilon_{\mathrm{h}} h_z(h_y r_x{}^0 - h_x r_y{}^0)}{2\hbar(\epsilon_{\mathrm{h}}{}^2 - \epsilon_{\mathrm{g}}{}^2)} \left\{1 - 3\left(\frac{\Delta r}{r}\right)^2\left(1 + \frac{\mathbf{h}\cdot\mathbf{r}^0}{\mathbf{h}\cdot\Delta\mathbf{r}}\right)\right\} \tag{53}$$

As eq 52 is identical with eq 33 except for $\mathcal{H}_{\mathrm{p}}$ replacing $\mathcal{H}$, it follows that the expressions for the reduced ICD for various guest degeneracies are identical with those of eq 35–42, with $\mathcal{H}_{\mathrm{p}}$ replacing $\mathcal{H}$. The conditions of host parametrization and sign correlations are unchanged, except in that the sign of $\mathcal{H}_{\mathrm{p}}(\epsilon_{\mathrm{g}})$ depends on the ratio $\Delta r/r$.

It is only possible to develop meaningful sign correlations for partially intercalated systems with $n > 2$ hosts if (i) $\Delta r/r << 1$ for which $\mathcal{H}_{\mathrm{p}}(\epsilon_{\mathrm{g}}) \simeq \mathcal{H}(\epsilon_{\mathrm{g}})$, or (ii) $\Delta r/r \gg 1$ for which $\mathcal{H}_{\mathrm{p}}(\epsilon_{\mathrm{g}}) \simeq -3(\Delta r/r)\mathcal{H}(\epsilon_{\mathrm{g}})$, or (iii) there is a dominant host transition for which $\Delta\epsilon << \epsilon_{\mathrm{g}} \sim \epsilon_{\mathrm{h}}$ such that

$$\mathcal{H}_{\mathrm{p}}(\Delta\epsilon) \simeq \mathcal{H}(\Delta\epsilon)\{1 - 3(\Delta r/r)^2(1 + \mathbf{h}\cdot\mathbf{r}^0/\mathbf{h}\cdot\Delta\mathbf{r})\}$$

In (i), the sign correlations of the fully intercalation case apply; for (ii) the sign correlations are reversed; for (iii) the sign correlations are those of $\mathcal{H}(\Delta\epsilon)$ if the quantity in braces is positive, and reversed if it is negative.

Host System with $n = 2$. For C_2 hosts under the restrictions discussed earlier, the ICD expressions follow directly from substitution of eq 32 into eq 28. For singly degenerate guests

$$\bar{R}_{\mathrm{g}}(x) = \mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{x})/r^3 \tag{54}$$

$$\bar{R}_{\mathrm{g}}(y) = -3\frac{\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{y})}{r^3}\left(\frac{\Delta r}{r}\right)^2 \tag{55}$$

$$\bar{R}_{\mathrm{g}}(z) = -\frac{\mathcal{H}^*(\epsilon_{\mathrm{g}}{}^{z})}{r^3}\left(1 - 3\left(\frac{\Delta r}{r}\right)^2\right) \tag{56}$$

Generalizations are possible here, for the x–z sign correlations are preserved provided $|\Delta r/r| < 1\sqrt{3}$. For larger Δr, $\bar{R}_{\mathrm{g}}(z)$ has the same sign as $\bar{R}_{\mathrm{g}}(x)$, but $\bar{R}_{\mathrm{g}}(y)$ (which vanishes for full intercalation) becomes appreciable with a sign opposite from that of $\bar{R}_{\mathrm{g}}(x)$ and $\bar{R}_{\mathrm{g}}(z)$.

The results for doubly degenerate guests may be derived in a similar fashion.

Parametrization in Terms of the Host Exciton CD

In the fully intercalated case, it is frequently possible to relate the host factors appearing in the ICD expressions to the exciton CD of the host transitions themselves. This relationship is most readily derived by considering the host CD directly.

Consider the host to comprise n identical chromophores H_i ($i = 1, \ldots, n$) as before, each with wave functions $|h\rangle_i$ (ground state $|0\rangle_i$) of energy ϵ_{h} relative to the ground state. The discussion is initially restricted to the $n > 2$ case, with the $n = 2$ considered later. Upon defining the product states

$$|0\rangle = |0\rangle_1 \ldots |0\rangle_n$$

and

$$|i\rangle = |0\rangle_1 \ldots |h\rangle_i \ldots |0\rangle_n$$

the overall wave functions of the host system for the states that are electric dipole allowed from the ground state may be written (using standard exciton and symmetry arguments[15-17]) in the form

$$|A_{\mathrm{h}}\rangle = (1/\sqrt{n})\sum_i |i\rangle$$

(singly degenerate and z-polarized from the ground state $|0\rangle$) and

$$|E_{\mathrm{h}}\rangle = (1/\sqrt{n})\sum_i e^{2\pi 1i/n}|i\rangle$$

$$|E_{\mathrm{h}}{}^*\rangle = (1/\sqrt{n})\sum_i e^{-2\pi 1i/n}|i\rangle$$

(double degenerate and xy-polarized from the ground state).

The CD of the z-polarized transition is readily shown to have the usual form

$$R(A_{\mathrm{h}}) = \frac{1}{n}\frac{\epsilon_{\mathrm{h}}}{2\hbar}\sum_{ij}\mathbf{h}_i \cdot \mathbf{r}_j{}^0 \times \mathbf{h}_j = -[R(E_{\mathrm{h}}) + R(E_{\mathrm{h}}{}^*)] \tag{57}$$

Exploiting the host symmetry, $R(A_{\mathrm{h}})$ may be written in the form

$$R(A_{\mathrm{h}}) = \frac{\epsilon_{\mathrm{h}}}{2\hbar}\mathrm{h}_1 \cdot \sum_j \mathbf{r}_j \times \mathrm{h}_j = \frac{\epsilon_{\mathrm{h}}}{2\hbar}\mathbf{h}_1 \cdot \sum_\xi C_n{}^\xi(\mathrm{r}_1^0 \times \mathrm{h}_1)$$

as the n rotation operators $C_n{}^\xi$ ($\xi = 1, \ldots, n$) will generate the entire set ($\mathbf{r}_j \times \mathbf{h}_j$). Noting that

$$\sum_\xi C_n{}^\xi(\mathbf{r}_1 \times \mathrm{h}_1) = n[0;0;(r_x{}^0 h_y - r_y{}^0 h_x)]$$

with the subscript 1 again implied in the definition of the vector elements, it follows that

$$R(A_{\mathrm{h}}) = (\epsilon_{\mathrm{h}}/2\hbar)n(h_z(h_y r_x{}^0 - h_x r_y{}^0)) \tag{58}$$

The definition of the host parameter $\mathcal{H}(\epsilon_{\mathrm{g}})$ of eq 34 may now be expressed in terms of $R(A_{\mathrm{n}})$ as

$$\mathcal{H}(\epsilon_{\mathrm{g}}) = \sum_h R(A_{\mathrm{h}})/(\epsilon_{\mathrm{h}}{}^2 - \epsilon_{\mathrm{g}}{}^2) \tag{59}$$

For the $n = 2$ case, the two exciton states that are electric dipole allowed are both singly degenerate, and have the form

$$A_{\mathrm{h}}(\pm) = (1/\sqrt{2})(|1\rangle \pm |2\rangle)$$

---

(15) Mason, S. F. *Inorg. Chim. Acta Rev.* **1968**, *2*, 89.

(16) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.

(17) Craig, D. P.; Walmsley, S. H. "Excitons in Molecular Crystals"; W. A. Benjamin: New York, 1968.

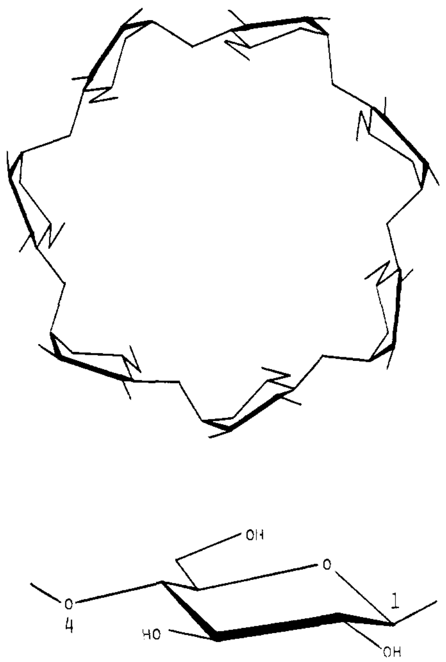

Figure 3. The cavity structure of β-cyclodextrin (above). Each individual unit has the structure of the glucose residue shown (below).

with $|A_h(+)\rangle$ z-polarized from the ground state and $|A_h(-)\rangle$ polarized in some symmetry undetermined direction in the xy plane. Then

$$R(A_h(+)) = -R(A_h(-)) = -(\epsilon_h/\hbar)h_z h_x r_y^0 \qquad (60)$$

In this case

$$\mathcal{H}^*(\epsilon_g) = \frac{1}{2}\sum_{\substack{\text{transitions}\\ h}} \frac{R(A_h(+))}{(\epsilon_h^2 - \epsilon_g^2)} \qquad (61)$$

Applications to Cyclodextrin Inclusion Complexes

The formalism of the previous sections has been developed in a general way without recourse to physical examples in order to emphasize that the conditions for sign correlations have an underlying symmetry basis. The only restrictions on the electronic structure of the host are those leading to the reduction of $\mathcal{H}(\epsilon_g)$ to $\mathcal{H}(0)$ or $\mathcal{H}(\Delta\epsilon)$. We can now turn to the most gratifying aspect of the paper: the direct application of these results to real systems. Three applications, corresponding to quite different combinations of these restrictions, will now be considered.

There has been considerable interest in applying the coupled-oscillator model to β-cyclodextrin inclusion complexes.[3,5-7] β-Cyclodextrin is composed of seven α-1,4-linked D-glucose residues, and thus has C_7 point symmetry. Guest molecules may be held in the cavity (Figure 3), forming inclusion complexes by intercalating along the C_7 axis. Data concerning the intercalation geometry could be useful in understanding synthesis and degradation reactions (both achiral and chiral) that the cyclodextrin catalyzes on some guests when they are included in its cavity. Previous work has supported the relevance of the coupled-oscillator model in describing the ICD of the guest transitions, but without exploiting the symmetry aspects of the problem, detailed calculations on the entire guest/host system are required for each guest examined.

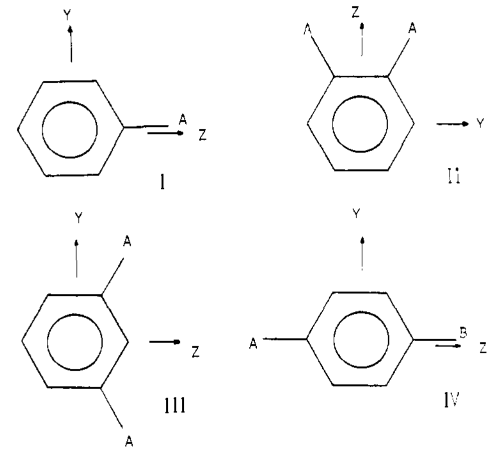

Figure 4. Definition of guest axes for substituted benzenes of C_{2v}, D_{2h} symmetry.

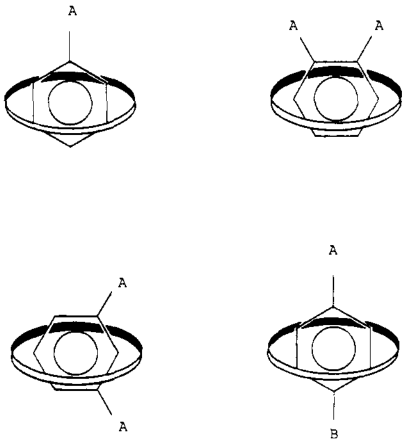

Figure 5. Intercalation modes predicted through the sign of the ICD.

Table I

guest[a]	point group	ref[b]	transition polarization	sign of CD	orientation predicted by $\mathcal{H}(0) < 0$[c]
IV A = OH, B = OH	D_{2h}	5	Z (B_{1u}) Y (B_{2u})	+ −	$Z = z$ $Y \perp z$
IV A = NH_2, B = NH_2	D_{2h}	5	Z (B_{1u}) Y (B_{2u})	+ −	$Z = z$ $Y \perp z$
IV A = NO_2, B = NH_2	C_{2v}	4, 5	Z (A_1) Y (B_2)	+ −	$Z = z$ $Y \perp z$
IV A = NO_2, B = OH	C_{2v}	4	Z (A_1) Y (B_2)	+ −	$Z = z$ $Y \perp z$
I A = OH	C_{2v}	4	Z (A_1) Y (B_2)	+ −	$Z = z$ $Y \perp z$
I A = NH_2	C_{2v}	4	Z (A_1) Y (B_2)	+ −	$Z = z$ $Y \perp z$
III A = OH	C_{2v}	5	Z (A_1) Y (B_2)	− +	$Z \perp z$ $Y = z$
III A = NH_2	C_{2v}	5	Z (A_1) Y (B_2)	− +	$Z \perp z$ $Y = z$
II A = OH	C_{2v}	5	Z (A_1)	+	$Z = z$
II A = NH_2	C_{2v}	5	Z (A_1)	+	$Z = z$

[a] See Figure 4. [b] The references are for the data given in columns 4 and 5. [c] These orientations are depicted in Figure 5.

The work of the previous sections shows that these detailed calculations may be circumvented by the explicit symmetry adaptation of the coupled-oscillator model. In particular, for C_{2v} and D_{2h} guests such as the substituted benzenes (Figure 4), the ICD is given by eq 33. The saturated nature of the cyclodextrin host leads to $\epsilon_h \gg \epsilon_g$ as a good first approximation, so that

$$\mathcal{H}(\epsilon_g) \simeq \mathcal{H}(0)$$

and the reduced ICD of a (γ)-polarized guest transition is given by eq 35, leading to the sign correlations of eq 36.

Application of these sign correlations to the guests of Figure 4 is summarized in Table I, in which the sign of $\mathcal{H}(0)$ is taken to be negative based on the *assumption* that the first para-substituted guest in the table will intercalate as illustrated in Figure

Table II

guest[a]	ref[b]	polarization	$R \times 10^{40}$/ cgs	$\bar{\nu} \times 10^{-3}$/ cm^{-1}	D/ Debye	$-\Delta$
IV	5	Z	0.52	45.3	4.35	0.3
A = OH, B = OH		Y	−0.72	34.6	2.35	
IV	5	Z	0.86	41.5	13.61	0.1
A = NH_2, B = NH_2		Y	−1.46	32.8	2.59	
IV	4, 5	Z	9.14	26.3	27.51	1.5
A = NO_2, B = NH_2		Y	−5.37	44.1	8.15	
IV	4	Z	7.50	31.6	20.23	1.1
A = NO_2, B = OH		Y	−3.83	44.1	8.15	
I	4	Z	0.16	47.4	6.26	0.1
A = OH		Y	−0.34	37.0	1.37	
I	4	Z	0.55	43.5	8.00	0.3
A = NH_2		Y	−0.24	35.6	1.15	
III	5	Z	−0.14	42.0	7.53	3.8
A = NH_2		Y	0.12	34.6	2.04	

[a] See Figure 4. [b] The references are for the data given in columns 3, 4, 5, and 6.

5. The remaining intercalation geometries (the last column of Table I) are then those predicted from the measured ICD assuming $\mathcal{H}(0) < 0$. The prediction that, for the mono- and para-substituted guests, the guest long-axis coincides with the host C_n axis is in accord with the expected mode of intercalation using molecular models. For the ortho-substituted guests, the ICD predicts an intercalation geometry in which both substituents remain on the same side of the host ring, whereas the meta-substituted guests favor the geometry in which the host ring effectively fits between the substituents (Figure 5). The latter results are not immediately obvious from studies of molecular models and illustrate the potency of the sign correlative procedure.

A note of caution should be added, however, in that the above assumes full intercalation. If the meta-substituted guests partially intercalate with the two groups remaining on the same side of the cyclodextrin ring, then the results of eq 53 apply, and the sign correlations persist only if $\Delta r/r$ is small.

Quantitative applications are hampered by a number of experimental factors, as well as the assumption that $\mathcal{H}(\epsilon_g) \simeq \mathcal{H}(0)$ is relatively insensitive to ϵ_g. Comparison of the ICD of different guests is made difficult by the range in equilibrium constants for the intercalation process. This problem is bypassed when the ICD of two different transitions on a single guest are compared. Consider, for example, a z-polarized and a y-polarized transition on the same guest. Then

$$\Delta = \frac{\bar{R}(z)}{\bar{R}(\gamma)} = -2\frac{\mathcal{H}(\epsilon_g{}^z)}{\mathcal{H}(\epsilon_g{}^y)} \simeq -2 \tag{62}$$

if $\mathcal{H}(\epsilon_g{}^z) \simeq \mathcal{H}(\epsilon_g{}^y) \simeq \mathcal{H}(0)$ or $\epsilon_g{}^z \simeq \epsilon_g{}^y$. (For sign correlations it is sufficient that $\mathcal{H}(\epsilon_g{}^z)/\mathcal{H}(\epsilon_g{}^y) > 0$.) The quantitative prediction of eq 62 may be tested by determining the ratio Δ from experimental estimates of the reduced ICD. However, for $\epsilon_g{}^z \simeq \epsilon_g{}^y$ (one of the conditions for which eq 62 should hold), the opposite sign of the ICD bands leads to some mutual cancellation, so that the *measured* values of $[R_g(\gamma)|$ will generally be too small. In addition, overlap of the bands in normal absorption leads to appreciable uncertainties in determining the $g_y g_y$. The results are summarized in Table II, in which the Δ estimated from the experimental quantities is shown to range from −3.8 to −0.1. The seemingly poor agreement is probably more the result of uncertainty in extracting the individual ICDs from the experimental data than of the assumption that $\mathcal{H}(\epsilon_q) \simeq \mathcal{H}(0)$, which incidentally will also cause deviation from the "ideal" ratio. (For example, values of Δ closest to −2 (viz. −1.5 and −1.1) are for guests with well-separated ICD bands (separations of about 16000 and 13000 cm^{-1}, respectively), where the effect of ICD band overlap is minimized.) These results therefore highlight the difficulties of *quantitative* parametrization from both a theoretical standpoint *and* from the standpoint of using experimental estimates of the guest parameters. Note, however, that the ratio has a constant sign, supporting the soundness of the sign correlation procedure.

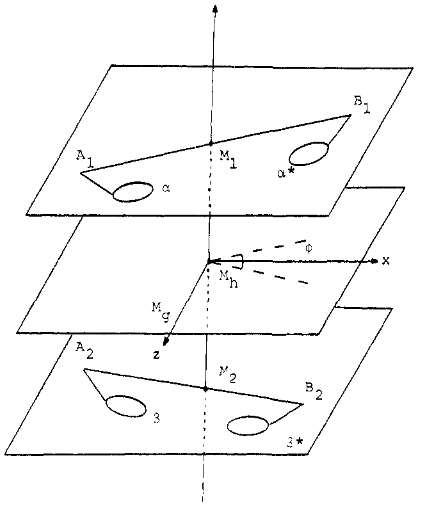

Figure 6. Definition of coordinate systems for guest intercalating along the host z axis.

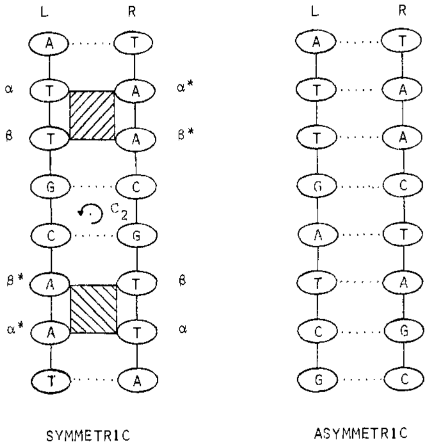

Figure 7. Diagrammatic representations of the symmetric (palindromic) and asymmetric (random) sequences.

Applications to Dye/DNA Systems

The process by which molecules intercalate into DNA involves a twist of the DNA helix,[1] resulting in a pocket between two base pairs which is particularly suited to slotting in planar aromatic guests. Intercalation may therefore be expected to occur along a local z axis, defined to bisect the normals to the lines connecting the points A_1 and B_1, A_2 and B_2, at which the individual bases are connected to their respective ribose chains (see Figure 6). The host system as seen by a particular guest molecule is assumed to comprise only two separate chromophores H_1 (the A_1, B_1 system with origin M_1) and H_2 (the A_2, B_2 system with origin M_2). The more distant base pairs are neglected because of the r^{-3} falloff of the interaction operator coupling the guest to the individual host chromophores, as are the effects of the ribose chain. Flat guests usually align parallel to the base pairs, which are themselves perpendicular to the helix axis (y).[4]

The work of the preceding sections leads to simple sign correlations only if the z axis is also a local symmetry axis. For most DNA intercalation sites, such a symmetry axis does not exist. In the work that follows, however, it will be shown that under certain conditions, the ICD may be recast in a form in which the DNA *acts* as a host with each intercalation site having a rigorous local C_2 symmetry.

Only base pairs of the type A–T, T–A, G–C, and C–G (using the usual nomenclature) are possible. Thus for any base α, its conjugate α^* with which it is paired is uniquely defined. A base pair may then be identified by specifying the base on only one strand, which we will take conventionally to be the left (L) strand with the helix schematically depicted as a flat sheet as in Figure 7. Thus an intercalation site with base pair α–α^* above and β–β^* below may be denoted $[\alpha\beta]$.

Two types of sequences are possible, as depicted in Figure 7. The *symmetric* (or palindromic) sequence comprised two identical strands, the right (R) strand being generated by a C_2 rotation of the L strand. This restricts the L strand to having the form $\{\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_3^*, \alpha_2^*, \alpha_1^*\}$. The *asymmetric* sequence comprises two strands that are conjugates (by definition), but have no such symmetry relationship. The ICD for these two different sequence types takes two distinct forms, and we consider them in turn.

ICD for Symmetric Sequences. The importance of the symmetric sequence is that, because of the C_2 symmetry of the flat sheet representation, for each $[\alpha\beta]$ site in the top part of the polymer, there will be a corresponding $[\beta^*\alpha^*]$ site in the bottom half. Although this C_2 axis does not exist in the real helical structure, the fact that intercalation is based on the *local* structure of an intercalation site leads to an equivalence of the sites $[\alpha\beta]$ and $[\beta^*\alpha^*]$ *except* that the local structure of $[\beta^*\alpha^*]$ is that of $[\alpha\beta]$ rotated by a C_2 rotation about the local z axis. If the guest has itself a C_2 axis aligned along the local z axis, then these sites will be rigorously equivalent. We restrict consideration here to such a case, for which

$$P_{\alpha\beta} = P_{\beta^*\alpha^*} \tag{63}$$

where $P_{\alpha\beta}$ is the probability of the guest intercalating into site $[\alpha\beta]$. Denoting the ICD of the guest in this site as $R(\alpha\beta)$, the total ICD per guest molecule may be written

$$R = \sum_{[\alpha\beta]} \frac{n_{\alpha\beta}}{2n} P_{\alpha\beta}\{R(\alpha\beta) + R(\beta^*\alpha^*)\} \tag{64}$$

$$R = \sum_{[\alpha\beta]} \frac{n_{\alpha\beta}}{2n} P_{\alpha\beta}\{R(\alpha\alpha^*) + R(\beta^*\beta)\} \tag{65}$$

where $n_{\alpha\beta}$ is the number of sites of type $[\alpha\beta]$, n the total number of sites, and (for the symmetric sequence) $n_{\alpha\beta} = n_{\beta^*\alpha^*}$. Equation 65 followed from eq 64 by noting that each base pair contributes independently to the ICD (in the order of perturbation theory used herein). Thus R formally reduces to a sum of contributions, *each* of the form $R(\alpha\alpha^*)$; i.e., R reduces to a sum of ICD's within intercalation sites (α–α^* above, α^*–α below) which have rigorous C_2 symmetry along the local z axis.

At this stage, it is worth considering the form of an individual $R(\alpha\alpha^*)$ in a little more detail. Noting that the in-plane polarized π–π^* transitions of the base pair system will couple most strongly with the guest (because of their lower energy), we have that $\mathbf{h}_1 \cdot \mathbf{r}_1 = 0$ for all the relevant host transitions. Thus the results of eq 43–51 (full intercalation) and eq 54–56 (partial intercalation) are directly applicable. Denoting by $\mathcal{H}^*_{\alpha\alpha^*}(\epsilon_g)$ the host parameter for the site $[\alpha\alpha^*]$, the reduced ICD for a nondegenerate guest in such a site has the form

$$\bar{R}(x) = (1/r^3)\mathcal{H}^*_{\alpha\alpha^*}(\epsilon_g) = -\bar{R}(z) \tag{66}$$

thus differentiating directly between intercalation modes. (The parametrization in this case results from approximating the host factor above as a sum over the individual $\mathcal{H}^*(\Delta\epsilon)$'s for the various π–π^* transitions of the base pair α–α^*.)

The total reduced ICD requires summation over all the intercalation sites, and has the form

$$\bar{R} = \pm \sum_{[\alpha\beta]} \frac{n_{\alpha\beta}P_{\alpha\beta}}{2nr^3}[\mathcal{H}^*_{\alpha\alpha^*}(\epsilon_g) + \mathcal{H}^*_{\beta^*\beta}(\epsilon_g)] \tag{67}$$

where the + applies to x intercalation and − to z intercalation of the relevant guest transition moment.

ICD for Asymmetric Sequences. Although sign correlations are rigorously expected on symmetry grounds only for the symmetric sequence DNA, there are two conditions for the asymmetric sequences when the sign correlations may be expected to persist: (i) if $n_{\alpha\beta} \simeq n_{\beta^*\alpha^*}$ and the guest has a C_2 axis along the host z axis; (ii) if there are the same number of base pairs α–α^* as there are of α^*–α *and* the intercalation is totally random (i.e., not site specific). Both these conditions allow the major contribution to the ICD to be written in terms of contributions from intercalation sites of C_2 symmetry. Condition (ii) corresponds to that invoked in the earlier paper[2] and is here seen to be directly deducible from the more general symmetry arguments presented herein.

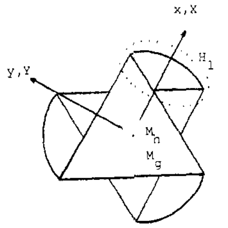

Figure 8. Coordinate system for tris(bidentate) complex (see text).

The experimental agreement, as discussed in the earlier paper,[2] is again uncannily good. The guests studied are all nondegenerate but with uniquely determined symmetry axes. In addition, the results for partial intercalation (eq 54–56) are particularly simple in this case, leaving the reduced ICD of x-polarized guest moments unchanged, but leading to the appearance of a reduced ICD for a y-polarized transition (at the expense of the z-polarized ICD) which vanishes in the full intercalation limit. This appearance of y-polarized ICD may therefore be used as a probe of partial intercalation in the context of our model.

Finally, an interesting spinoff from these results is that the ICD n turn may be used as a probe of general features of the DNA structure. The very existence of the sign correlations implies that the DNA used in the studies must conform to either a symmetric sequence or to one of the two conditions for asymmetric sequences discussed above. Although the present amount of data is insufficient for such use, systematic studies in the future could lead to not only definition of the intercalation modes, but also further information about local and global aspects of the DNA polymer itself.

Application to Metal Chelate Complexes of C_n, D_n Symmetry

In the preceding applications, the host and guest systems are distinct molecular species. The known polarizations of the guest transitions lead to the ICD being a direct probe of the intercalation geometry. We now consider a case where the guest and host systems are simply different chromophoric systems within the same molecule. In such a case, the host–guest geometry is known, and the ICD may be used to assign the polarization of the guest transitions if the host properties are known, illustrating the versatility of the model.

The systems we consider here have been discussed in some detail elsewhere, but the original paper contains an error of sign.[13] Thus we take this opportunity to both correct the sign and illustrate how easily the results flow from the general model of this paper. In tris(bidentate) metal complexes of D_n, C_n symmetry, the chelate system may be considered as an n-fold multichromophoric host system (each chelate being separate host chromophore) of overall D_n, C_n symmetry. Electric dipole allowed d–d transitions and charge-transfer transitions involving only the metal-ligating atom system are assumed to have metal-centered transition moments, thus constituting an achiral guest system which is assumed to have negligible electron exchange with the chelate system. (The relevance of this assumption is discussed elsewhere.[13])

The symmetry of the guest must contain that of the host as a subgroup, and may be taken as D_{3d}. The guest and host axes must therefore coincide, ensuring diagonality of the guest tensor in the host system. It follows from eq 38 that the reduced ICD of an electric dipole allowed z-polarized guest transition (A_2 symmetry) and of an electric dipole allowed xy-polarized guest transition (E_u symmetry) are given by (see Figure 8)

$$\bar{R}(z) = -(2/r^3)\mathcal{H}(\epsilon_g^{\,z}) \tag{68}$$

$$\bar{R}(xy) = +(2/r^3)\mathcal{H}(\epsilon_g^{\,xy}) \tag{69}$$

For unsaturated chelates, the host parameter may be assumed to be dominated by a single, long-axis polarized π–π^* transition on each of the separate host chromophores, so that, using eq 37, 58, and 59, we have

$$\bar{R}(z) = -(2/r^3)R(A_h)/\left(\epsilon_h^2 - \epsilon_g^{z^2}\right) \qquad (70)$$

$$\bar{R}(xy) = +(2/r^3)R(A_h)/\left(\epsilon_h^2 - \epsilon_g^{xy^2}\right) \qquad (71)$$

where $R(A_h)$ is the exciton CD of the A_2 transition of the host system. Thus a z-polarized guest transition will have an ICD of sign *opposite* to that of the z-polarized host system transition, and an xy-polarized guest transition will similarly have a sign opposite to that of the CD of the host E_u transition. This is exactly opposite to the conclusion of the earlier paper, which stands corrected by eq 70 and 71 above.

If the polarizations of the guest transitions are known from an independent experiment (e.g., polarization studies in normal absorption), then the ICD may be used as a stereochemical probe, in that the absolute configuration may then be determined by the sign of the host exciton CD band corresponding to the A_2 transition. Similar conclusions are possible for saturated chelate systems, when the host parameter may be approximated by $\mathcal{H}(0)$. In this case, the host parameter is best determined parametrically for a complex in which all the other quantities are known, and then transferred to applications to other metal complexes with the same chelate systems.

Conclusions

Sign correlations or sector rules have enjoyed a wide populatiry in relating CD spectra to stereochemical factors. Many sector rules are empirically based, but suffer from an inability to predict when they will fail. The sign correlations developed in this paper in terms of a well-defined model will fail only when the well-defined restrictions or assumptions of the model are not relevant to the system under consideration. This failure immediately becomes a positive aspect of our approach, as it can be directly interpreted in terms of physical characteristics of the interacting systems and the intercalation process. It is not sufficient that a theoretical model predict a set of sector rules or sign correlations; it is crucial that it also (i) yield a quantitative description of the CD intensities observed experimentally, and (ii) be capable or predicting why and when the sign correlations or sector rules will fail.

Acknowledgment. The authors would like to thank Professor Bengt Nordēn for the introduction to dye/DNA systems, and Dr. Tom Kurucsev for discussions on the cyclodextrin systems.

Registry No. I (A = OH), 108-95-2; I (A = NH_2), 62-53-3; II (A = OH), 120-80-9; II (A = NH_2), 95-54-5; III (A = OH), 108-46-3; III (A = NH_2), 108-45-2; IV (A = OH; B = OH), 123-31-9; IV (A = NH_2; B = NH_2), 106-50-3; IV (A = NO_2; B = NH_2), 100-01-6; IV (A = NO_2; B = OH), 100-02-7; β-cyclodextrin, 7585-39-9.

Conformational Mobility in the *trans*-Cycloheptene–Copper(I) Triflate Complex

Gregory M. Wallraff,[1a] Richard H. Boyd,[1b] and Josef Michl*[1a]

Contribution from the Departments of Chemistry and Chemical Engineering, University of Utah, Salt Lake City, Utah 84112. *Received December 29, 1982*

Abstract: The conformational properties of the copper(I) trifluoromethanesulfonate (CuOTf) complexes of (*E*)- and (*Z*)-cycloheptene and -cyclooctene have been studied by ^{13}C NMR. Both *cis*-cyclooctene·CuOTf and *trans*-cycloheptene·CuOTf show dynamic NMR behavior in the temperature range studied (30 to −117 °C) and yield values of ΔG^{*}_{173} = 7.8 kcal/mol and ΔG^{*}_{299} = 9.5 kcal/mol, respectively. The DNMR behavior of the *cis*- and *trans*-cyclooctene complexes as well as that of the *cis*-cycloheptene complex is very similar to that of the corresponding free olefins. It is now proposed that the seven nonequivalent ^{13}C NMR signals observed at low temperature for the *trans*-cycloheptene complex are due to an unsymmetrical chair conformation of the *trans*-cycloheptene ligand and that the dynamic process observed at higher temperatures involves a pseudorotation of the cycloheptene ring little affected by the complexed copper ion. Both molecular mechanics (MOLBD) and semiempirical quantum mechanical calculations (MNDO) on the free olefin find the unsymmetrical chair form to be an energy minimum and yield values for the free energy of activation which are in good agreement with the value experimentally determined for the complex.

Introduction

Conformational processes in cyclic hydrocarbons have been extensively investigated with both experimental and theoretical techniques. Dynamic ^{13}C and ^{1}H NMR (DNMR) are probably the most widely used analytical methods and are capable of giving reliable activation parameters for the process under study, provided sufficient care is taken in the treatment of the spectral data.[2] Total line-shape analysis is the method of choice for evaluating such data and can be applied to systems ranging from simple two-site exchange through complex multispin systems.[3]

Computationally, cyclic hydrocarbons have been most throughly studied using molecular mechanics (force field) calculations, which enable one to determine stable ground-state structures and map potential surfaces in a routine manner.[4] Semiempirical quantum mechanical methods have also been applied to the conformational analysis of cycloalkenes.[5] complementing, rather than competing with, the aforementioned calculations.

For some time we have been interested in the structural characteristics of molecules possessing strained double bonds.[6] *trans*-Cyclooctene is the smallest *trans*-cycloalkene which has been

---

[1] (a) Department of Chemistry. (b) Department of Chemical Engineering.

[2] (a) Jackman, L. M., Cotton, F. A., Eds.; "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1975. (b) Mann, B. E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 3, Chapter 20, p 89.

[3] Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411.

[4] (a) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161. (b) Ermer, O. "Aspekte von Kraftfeldrechnungen"; Wolfgang Baur Verlag: Munich, 1981. (c) Burkert, U.; Allinger, N. L., Eds. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; American Chemical Society Monograph 177.

[5] Favini, G.; Nava, A. *Theor. Chim. Acta* **1973**, *31*, 261.

[6] Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637.

0002-7863/83/1505-4550$01.50/0