

Coupled Oscillator Calculations of Circular Dichroism Intensities: Structural Applications in Organic Chemistry^a.

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Abstract. The DeVoe coupled-oscillator approach to the calculation of circular dichroism features is presented and discussed. Particular attention has been devoted to clarifying the importance of many-body effects in determining the optical activity. Significant examples of configurational and conformational assignment carried out by means of this technique are also discussed.

INTRODUCTION

The circular dichroism spectrum of a compound contains all the stereochemical information concerning that molecule: in fact, the energy position, sign and intensity of a single Cotton effect are dependant on the overall chemical structure and hence circular dichroism, and more in general chiroptical data, are potential reservoirs of structural information. However, the analysis of a circular dichroism spectrum^{1,2} very often does not allow definitive conclusions to be drawn on the molecular absolute stereochemistry, unless some significant feature (e.g. an exciton couplet^{1,2}) is present in the spectrum. On the other hand, synthetic organic chemists dealing with optically active molecules have need of simple and reliable methods for interpreting c.d. data in order to avoid long and tedious chemical correlations, which often have to be carried out to establish molecular absolute configurations. This problem has been approached several times in the literature and empirical methods such as the so called sector rules^{3,4} (see, for instance, the octant rule for the saturated carbonyl chromophore) have been proposed. Methods are also available which allow spectra-structure relationships to be established without any comparison with a reference molecule (non empirical methods).

It is in fact possible, once a given molecular geometry has been assumed, to calculate, for instance, the rotatory strength of a chosen transition employing two different groups of methods: the molecular orbital (MO) approach^{1,2,5} and independent-system (IS) approach^{1,2}. The former makes use of overall molecular wavefunctions to provide theoretical rotatory strengths to be compared with the experimental ones. The reliability of this method depends mainly on the quality of the wavefunction of the ground and excited states. This aspect can constitute a very difficult task in particular for molecules having complex structures:

^a Dedicated to the memory of Professor Gunther Snaatzke in recognition of his pioneering contribution to circular dichroism.

and represents a limitation for the general applicability of this technique. The latter approach is based on the so called independent-systems methods: i.e. in a chiral molecule, one (or more) chromophore, where the electronic transition under examination is localized, and one (or more) perturber which "modifies" the above transition, are separated. From the interaction chromophore/perturber(s) arises the optical activity. Among the independent-system techniques, those based on coupled oscillators or polarizability models have received considerable attention^{1,6}. Such models have been quite successful for molecules where two identical chromophores can be separated (e.g. 1,1-binaphthyl derivatives) or that absorb in the same range of wavelengths (for instance benzoates of aromatic alcohols). Generally, these approaches, are formulated in a quantum-mechanical frame^{1,2,6}, even if some procedures are known, like the DeVoe model⁷, which largely use the methods of classical physics. In this model, a molecule is considered to be composed of a set of sub-systems, the chromophores: they are polarized by the external electromagnetic radiation and are coupled each other by their own dipolar oscillating fields. The optical properties (absorption, refraction, optical rotatory dispersion and circular dichroism) of the molecule under study can be calculated taking into account the above interaction of the subsystems.

RESULTS AND DISCUSSION

a. The DeVoe polarizability approach

The DeVoe treatment of the optical properties of a molecule require a division of the molecule into a set of subsystems which have to be suitably characterized. Therefore, each subsystem is represented in terms of one (or more) oscillator: each oscillator represents an electric dipole allowed transition, defined by the polarization direction \bar{e}_i and the complex polarizability $\alpha_i(\bar{\nu}) = R_i(\bar{\nu}) + iI(\bar{\nu})$. $I_i(\bar{\nu})$ is obtainable from the experiment, i.e. from the absorption band of the compounds which can be considered good models of the subsystems, $R_i(\bar{\nu})$ can be calculated from $I_i(\bar{\nu})$ by means of a Kronig-Kramers transform. Under the external radiation, each sub-unit is polarized depending on the local electric field, this field being the incident field E_i plus the fields from polarizations of other sub-units:

$$1) \quad \begin{aligned} m_i &= \alpha_i(\bar{\nu}) (\text{component of the total field along } \bar{e}_i) = \\ &= \alpha_i(\bar{\nu}) [\bar{e}_i \cdot E_i - \sum_{j \neq i} G_{ij} m_j(\bar{\nu})] \\ G_{ij} &= (1/r_{ij})^3 [\bar{e}_i \cdot \bar{e}_j - 3(\bar{e}_i \cdot \bar{e}_j)(\bar{e}_i \cdot \bar{e}_j)] \end{aligned}$$

G_{ij} is the point-dipole point-dipole interaction term. This a system of linear equations, relating the induced moment on unit i (m_i) to the induced moments on all the other units. By solving this system, one can obtain the induced moment on each group as a function of the external field values at the dipole location:

$$2) \quad m_i(\bar{\nu}) = \sum_j A_{ij}(\bar{\nu}) E_j$$

where A is the inverse of matrix B , $B_{ij}=(\delta_{ij}/\alpha_i)+G_{ij}$. It is then possible to calculate electric polarization and the complex refractive indexes for left- and right-circularly polarized radiation, obtaining, after reliable approximations, the expression for the circular dichroism as:

$$3) \quad \Delta\epsilon(\tilde{\nu})=0.0073\pi^2 N\tilde{\nu}^2 \sum_{h,j}^N \theta_h \chi_h \beta_j A_{hj} \text{Im}A_j$$

where $\text{Im}A_{ij}$ means the imaginary part of the element A_{ij} . The DeVoe model is an exact treatment in the sense that the mutual action of dipoles, under the external radiation field, is taken into full account. This is because it gives an exact (all-order in G_{ij}) treatment of the molecular optical properties. The drawbacks are two: the first one is that a practical calculation involves inversion of B matrix at every frequency of interest and the dimension of B (which depends on the number of the dipoles) grows rapidly with molecular complexity. The second is that it is not so easy to establish when a coupled oscillator treatment is the adequate one: intrinsically dissymmetric systems exist and asymmetric molecules are expected, in general, to tend to such cases when higher and higher energy states are considered. It is possible to understand how two different units are coupled together due to the action of the external field: the two units are polarized by the external field, with values $E(1)$ at 1 and $E(2)$ at 2, respectively, plus the field due to the other polarized oscillator. To a first approximation, to describe the coupling one can think that osc.1 feels the external field+ the field of osc.2 perturbed by the external field only, and correspondingly, osc.2 feels the external field at 2 + the field of osc.1 perturbed by the external field only. To higher orders, one should include other coupling terms : for instance, one should consider that osc.1 feels also the field due to osc.2 perturbed by osc.1 only (the same is true for osc.2). Of course this back and forth process should continue ad infinitum, describing the total field at i using a series. The largest part of optical activity treatments retain only the first terms of this series (the external field+ the fields of all other oscillators perturbed by the external field only); thus they are first-order treatments in the interaction term G_{ij} . In the DeVoe model the use of a perturbation series is avoided, by solving the above system of linear equations and obtaining the matrix elements a_{ij} , at each frequency. Whilst first order treatments provide additive contributions to the optical activity of the chromophore coming from each perturber, additivity of perturber contributions cannot be expected in all-order treatments. Since higher order perturbative (and all-order) treatments introduce a more complete description of the interaction, in principle they have to be preferred to simple first-order models, in spite of a major computational effort. It is important to stress that in some cases these last techniques have to be used because the first order optical activity is zero. A molecule like (-)-(R)-1,3-dimethylallene can be used as an example. Within the DeVoe model this molecule can be represented, at the simplest level, in terms of three interacting polarizabilities (Fig. 1),

if we are interested in studying the optical activity of the electrically allowed ${}^1A_1 \rightarrow {}^1B_2$ transition of the allene chromophore. Owing to the symmetry of the chromophore and of the substituents, each couple of chromophore/perturber interacting dipoles is lying in a plane, giving zero contribution to CD).

b. A practical calculation: geometrical and spectroscopic input parameters.

In the case of the chiral alkylbenzene, (+)-(S)-2-phenyl-3,3-dimethylbutane 1, the CD and UV absorption in the 200-180 nm spectral region have been calculated⁸ in a DeVoe coupled-oscillator framework. The characteristics of the oscillators, which have to represent the polarizability allied to the aromatic moiety of the molecule, are derived from the experimental spectrum of toluene: hence toluene is here assumed as a chromophore simulating the effective aromatic one. Thus, toluene absorption band centered at 188 nm has been split into two components with polarization perpendicular and, respectively, parallel to the C_2 axis (in the local C_{2v} symmetry). A third transition at 204 nm, ${}^1A_1 \rightarrow {}^1A_1$ in character, is assumed to borrow its intensity from the above parallel and near-in-frequency ${}^1A_1 \rightarrow {}^1A_1$ transition. Finally, a further polarizability, orthogonal to the C_2 local-symmetry axis, has been introduced to take into account the observed toluene absorption at about 260 nm. All 4 dipoles are located at the centre of the phenyl ring. As far as the alkyl part is concerned, methane and 2-methylpropane have been assumed as suitable model chromophores for methyl and t-butyl groups, respectively. Thus, 3 dipoles, located on the tertiary carbon of t.butyl, the first parallel to local C_3 axis and the others perpendicular to the same axis, represent the absorption of methylpropane in the 165-110 nm range. In the essence, the experimental spectrum of 2-methylpropane down to 110 nm, ϵ_0 , is split into a parallel (to C_3 axis of t.butyl group) and two perpendicular dipoles according to the equations:

$$\epsilon_{\parallel} = \epsilon_0 \cos^2 \theta \quad ; \quad \epsilon_{\perp} = \epsilon_{\perp} = (\epsilon_0/2) \sin^2 \theta$$

with θ the angle between C-C bonds and C_3 axis. This partition of the vacuum UV absorption (which is the nearest in frequency to the aromatic absorption) is consequential to the assumption that local electronic excitations in the 110-165 nm spectral region can be represented by dipoles oscillating along the C-C bonds themselves. Consequently, in addition to the polarizabilities of t.butyl and methyl groups, already considered, the polarizability of the C-C bonds connecting the asymmetric carbon to the considered chromophores have also to be taken into account. Thus 3 dipoles on this carbon, each directed along a C-C bond from this carbon, centred at 134 nm and with the reasonable dipolar strength $2 D^2$, have been introduced. Using the above simplified model for the alkyl group polarizability both CD and UV absorption intensity, strictly comparable to the observed ones, have been calculated for the most probable molecular conformation of the asymmetric alkyl benzene studied. It must be observed that calculated CD intensity is also here mostly due to higher-order effects, *vide supra*, which become effective when polarizabilities on the asymmetric carbon are introduced: because their "bridge" location they amplify chiral interaction between alkyl and aromatic chromophores.

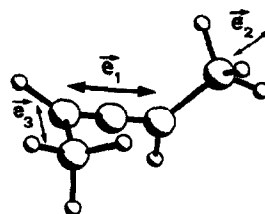


Figure 1 Structure of (-)-(R)-1,3-dimethylallene. The dipoles employed in the description of the system are indicated.

c. Perturbative approaches in the DeVoe frame.

In order to formulate more simple correlations between structure and CD properties, we use here the alternative approach of approximating the elements A_{ij} by perturbative methods. This approach presents the further advantage that a physical insight into the origin of optical activity is easily gained. Then:

$$4) \quad A_{ij} = \alpha_i(\bar{\nu}) G_{ij} \alpha_j(\bar{\nu}) + \sum_{k=1}^N \alpha_i(\bar{\nu}) G_{ij} \alpha_k(\bar{\nu}) G_{jk} \alpha_k(\bar{\nu}) + \dots$$

The first term of this series represents the polarization of unit i due to unit j polarized by the external field only (pairwise interactions⁹ or first order perturbation, this term gives rise to the so called first order optical activity), the second one is the polarization of unit i due to unit j , which, in turn, is perturbed by any unit k , polarized by the external field (three-way or second order perturbation). Using the perturbation method a direct relationship between the induced dipoles and the local external field values is provided. Therefore, the elements A_{ij} which are necessary to calculate the CD can be quite easily evaluated. In the simple case of a molecule constituted by two equal chromophores, (degenerate coupled oscillator system) having each only one electrically allowed transition, the above expansion is usually truncated to first order terms. In this way the evaluation of $\text{Im}A_{ij}$ as well as that of $\Delta\epsilon(\bar{\nu})$ is made easier and we have^{10,11}:

$$5) \quad \Delta(\bar{\nu}) = 0.029\pi^2 N \bar{\epsilon}_1 \chi \bar{\epsilon}_2 R_{12} G_{12} \bar{\nu}^2 I(\bar{\nu}) R(\bar{\nu}).$$

This formula is similar to those obtained in a quantum-mechanical frame^{1,2} and from it the origin of some spectral features (i.e., the exciton couplet present in the CD spectra of chiral dimeric molecules, like dibenzozates and so on) can be easily understood. In fact, $\Delta\epsilon(\bar{\nu})$ can be considered to derive from the product of a geometrical factor, $GF = \bar{\epsilon}_1 \chi \bar{\epsilon}_2 R_{12} G_{12}$, and a spectroscopic factor, $SF = \bar{\nu}^2 I(\bar{\nu}) R(\bar{\nu})$. GF is determined by

the relative disposition of the chromophores 1 and 2 and by the orientation of the transition moments $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ within the chromophores. The spectroscopic factor is the product of two functions $I(\bar{\nu})$ and $R(\bar{\nu})$. The former is an even function with respect to $\bar{\nu}_{max}$, whilst the latter is an odd function with respect to the same value. The product of these functions will be an odd function having the typical couplet shape. Therefore the sign of the couplet will be determined by the value (positive or negative) of GF .

In the case of two different oscillators, we have:

$$6) \quad \Delta\epsilon(\bar{\nu}) = 0.014\pi^2 N \bar{\nu}^2 (\bar{\epsilon}_1 \chi \bar{\epsilon}_2) R_{12} G_{12} [I_1(\bar{\nu}) R_2(\bar{\nu}) + I_2(\bar{\nu}) R_1(\bar{\nu})]$$

If the absorption ranges of the two oscillators are well separated on the frequency scale we have two distinct Cotton effects: one centered in the absorption range of the chromophore 1 and the other one corresponding to the absorption range of the chromophore 2. The signs of the two CD bands are determined by $GFI_1(\bar{\nu})R_2(\bar{\nu})$ (in the first absorption region) and by $GFI_2(\bar{\nu})R_1(\bar{\nu})$ (in the second absorption region). Notice that, in a sense, the previous couplet has been now split in a positive and a negative branch, each of them

centered at the absorption frequency of each chromophore. As an example of a calculation, we describe here the evaluation of the CD allied to the lowest energy $\pi \rightarrow \pi^*$ transition of an optically active cis-diene chromophore, (-)-2,3-dimethylenenorbornane¹². This molecule can be considered as a cis-diene chromophore asymmetrically perturbed by a C-CH₃ bond. Each of these subgroups can be described by a single oscillator: the former one polarized along the line joining the terminal diene carbon atoms and the latter polarized along the C-CH₃ axis. As far as the values of $I_1(\bar{\nu})$ and $R_1(\bar{\nu})$ are concerned, a lorentzian polarizability of 25 D² centered at 250 nm gives a satisfactory representation of the absorption band of the cis-diene chromophore, whilst to describe the polarizability of the C-CH₃, previous work showed that a lorentzian polarizability of 2D² at 134 nm was reasonable. The geometrical parameters used in the calculations are summarized in Fig. 2.

A $\Delta\epsilon$ value of -0.57 is calculated at 250 nm, to be compared with an experimental value of -0.63, indicating an excellent agreement between theory and experiment.

As it has been recently shown^{13,14} the CD of the ${}^1A_1 \rightarrow {}^1B_2$ transition of 1,3-dimethylallene, $\Delta\epsilon(\bar{\nu})$ can be very easily calculated to 2nd order, within the simple polarizability model presented in sec. a-c, employing the expansion of A_{ij} of eq. 4. A family of structurally related compounds is that of cyclohexylidenemethanes: Gedanken and Walborsky have recently reported¹⁵ and discussed the CD data of (-)-(R)-(4-methyl-cyclohexylidene)ethane. For the above molecule, which can be schematized as reported below:

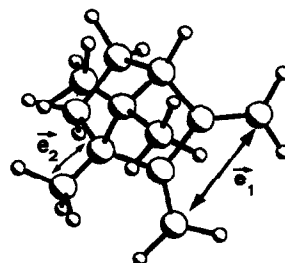
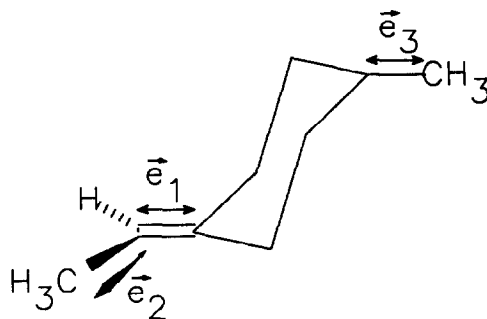


Figure 2 Structure of (-)-2,3-dimethylenenorbornane and the dipoles representing the interacting subsystems.



i.e. with three oscillators: \bar{e}_1 for the olefin chromophore, \bar{e}_2, \bar{e}_3 for the C-CH₃ perturbors. The formula which provides CD as a frequency dependent function is the same as previously reported¹⁴, owing to the similar structural relationships in the two cases:

$$\Delta\epsilon(\bar{\nu}) = -0.014\pi^2 N \bar{\nu}^2 (\bar{e}_2 \times \bar{e}_3) \bar{R}_{23} G_{12} G_{13} I_1(\bar{\nu}) R^2(\bar{\nu})$$

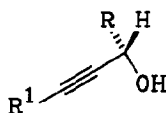
a negative CD can be calculated, as experimentally observed for the (R) absolute configuration. These

results show that even complex molecules can be treated by simple equations.

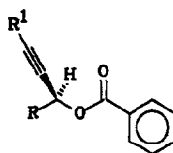
OTHER SIGNIFICANT APPLICATIONS IN ORGANIC STEREOCHEMISTRY.

a. Absolute configuration of acetylenic carbinols.

Compounds having general formula



constitute an important class of intermediates in the synthesis of natural products. In spite of this fact, only the empirical method of Mori and Akao¹⁶ for determining their absolute configuration was known. The main obstacle to the use of CD spectroscopy is due to the fact that these molecules do not absorb in the spectral range 185-600 nm, accessible to the commercial instruments. In order to introduce an accessible chromophoric system, these alcohol were transformed¹⁷ in to the corresponding benzoates which show the well known $\pi \rightarrow \pi^*$ electrically allowed transition at 230 nm. They all show a positive Cotton effect with $\Delta\epsilon$ between +1 and +3. Taking into account the most stable conformation of simple benzoates proposed¹⁸ by Brewster and assuming arbitrarily the S absolute configuration for the chiral center, the following structure can be used for a DeVoe treatment.

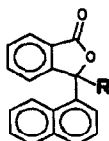


The 230 nm transition of the benzoate chromophore was described in terms of a single oscillator polarized along the line joining the carbonyl carbon atom to phenyl group, the triple bond has been represented only by means of the ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition polarized along the axis of acetylenic function, while, for the alkyl groups the parameters set up previously^{8,13}, have been used¹⁷. In this way $\Delta\epsilon$ values, for the benzoate 230 nm transition, in the range between +1 and +2 are obtained, reproducing sign and intensity of the experimental values. Therefore a non empirical correlation between the S absolute configuration of the chiral center and a positive CD band at 230 nm in the spectrum of the acetylenic benzoate has been established. This correlation is quite general because it is independent of the nature of the substituent (R_1) of the acetylenic group. In fact, it will be valid for all the groups which do not change the polarization direction of this chromophore: i.e. a variety of substituents such as alkyl, acetylenic, cyano and halogens. The use of this rule has been successively extended¹⁹ to tertiary acetylenic alcohols, allowing to solve an interesting configurational problem. To the levorotatory antipode of 3-methyl-1-pentyn-3-ol, 2, was assigned the S absolute configuration, whilst the same configuration was assigned²⁰ to the dextrorotatory antipode of 3,4,4-trimethyl-1-pentyn-3-ol, 3: this last assignment gave rise to several inconsistencies in the stereochemistry of products

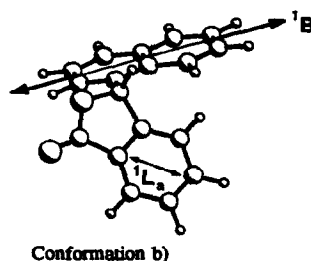
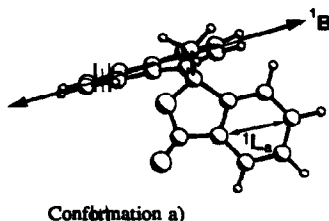
correlated to 3, such as allenes and acetylenes. Whilst the S absolute configuration can be safely attributed to (-)-2, owing to its chemical correlation to (+)-(S)-2-hydroxy-2-methylbutyric acid, the configurational assignment of (+)-3 appeared less certain, because it was established only by means of the Prelog rule. The two alcohols were then transformed¹⁹ in to the corresponding benzoates and the CD of the 230 nm transition, measured. The benzoate of (S)-2 showed positive CD at 230 nm, as expected following our CD-based correlation. On the contrary, the CD spectrum of the benzoate of the presumed (S)-3 showed a negative CD band in correspondence of the same transition, according to an R absolute configuration of the stereogenic center of the dextrorotatory antipode of 3. On this basis the data reported in the literature can be revisited and any difficulty eliminated.

b. Conformation of 3-(1-naphthyl)phthalides.

Compounds having the following structure:



were chromatographically separated (separation factor α in the range 1.15-2.5) by means of the chiral stationary phases derived from (S)-3,5-dinitrobenzoylphenylglycine and a chiral discrimination mechanism, by which the antipodes of these substances are separated on these phase, proposed²¹. With this mechanism it was also possible to explain why the structure where R is an alkyl group i.e. Me, Buⁿ, Prⁱ) is better separated than to the compound where R=H. Such a difference in behaviour has been attributed to a different conformation of the substituted systems (conformation a) with respect to the unsubstituted ones (conformation b).



The antipodes of the molecules which preferentially assume the structure a) are better "recognized" by the chiral phase and the resolution is more efficient. In order to demonstrate the existence of such different conformations, the circular dichroism spectra of the phthalide with R=Prⁱ (as representative of the 3-substituted compounds) and of the phthalide with R=H were measured and analyzed. The spectrum of the former compound does not show any couplet in the range (200-250 nm) where the coupling between the ¹B_u transi-

tion of the naphthalene chromophore and the 1L_a of the phthalide chromophore should occur: but only a single, positive (for the R absolute configuration) and intense ($\Delta\epsilon$ 70 ca.) band is observed. On the contrary a strong couplet (negative for the R absolute configuration) is found in the CD spectrum of the unsubstituted phthalide. A detailed analysis of the CD data has been carried out, by means of coupled oscillator calculations, in the DeVoe frame²². The 1B_u transition of the naphthalene chromophore has been described by means of a single dipole, located in the center of the naphthalene system and directed along the long axis of the chromophore. To it has been attributed a dipolar strength of 90 D² centered at 220 nm. The phthalide chromophore shows an allowed transition at 230 nm, polarized along the benzo-carbonyl bond axis. Thus, a single polarizability at 230 nm, directed as indicated and located in the center of the benzene ring, has been employed to describe this transition. Furthermore, other transitions in the phthalide chromophore have to be taken into account. In the spectrum of the benzoate chromophore (a good model of the phthalide moiety) an absorption band is observed at 195 nm (ϵ 40000 ca.). A CNDO/S-CI calculation on methyl benzoate gave, in addition to the 230 nm absorption band, a couple of quasi-degenerate excitation at 190 nm, lying in the aromatic plane and polarized along and perpendicularly to the benzene-carbonyl bond axis. Using the above dipoles, located in the center of the benzene ring, a good reproduction of the CD spectrum of alkyl-substituted phthalides has been obtained by means of conformation a), where the 1B_u and 1L_a transition dipoles are in practice parallel each other and then a CD couplet has not be expected. On the contrary, an intense negative couplet has been obtained for conformation b), in keeping with a structural situation where the above dipoles are no longer parallel. Therefore the analysis of the CD spectra allows to establish the prevailing conformation in solution for the two antipodes, supporting then the proposed chiral recognition mechanism.

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