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The Circular Dichroism and Absolute Configuration of *endo*-dicyclopentadiene

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Exciton theory has been applied to determine the absolute configuration of (—) endo-*dicyclopentadiene from its circular dichroism spectrum.*

Introduction

The $\pi \rightarrow \pi^*$ transition in mono-ethylenes is observed as a broad absorption band at around 180 mμ and, in general, has an oscillator strength of about 0.3.[1] This transition is electric dipole allowed and its electric transition dipole moment ($\rho \approx 3.4 \times 10^{-18}$ e.s.u.) is polarized along the bond axis. Provided there is negligible overlap between the two double bonds, the resultant absorption spectra of dienes can be interpreted in terms of exciton coupling,[2,3] and if the two double bonds are dissymmetrically disposed, the circular dichroism produced by exciton exchange provides a non-empirical spectroscopic method of determining the absolute configurations.[4]

The exciton model of optical activity has provided a reliable method for the assignment of the absolute configurations of simple organic molecules,[5] of oligomers and polymers[6,7,8,9] and of inorganic complexes.[10,11] We wish here to use the conclusion of this theory in order to determine the absolute configuration of a ligand which is of considerable current interest in inorganic chemistry, namely *endo*-dicyclopentadiene. The conformational rigidity and the fact that the (non-absolute) coordinates of the two double-bonds can be inferred with reasonable confidence makes the non-empirical assignment of the absolute configuration of the recently resolved[12,13] *endo*-dicyclopentadiene molecule a tractible problem.. The analytic expressions for the rotational strengths and the interaction between the transition dipole moments will be derived in a general way so that they are applicable to any coupled dissymmetric system containing two essentially degenerate chromophores.

It is convenient to specify the transition dipole vectors of the two double bands in terms of the angles α, β and γ for vector 1 and α', β' and γ' for

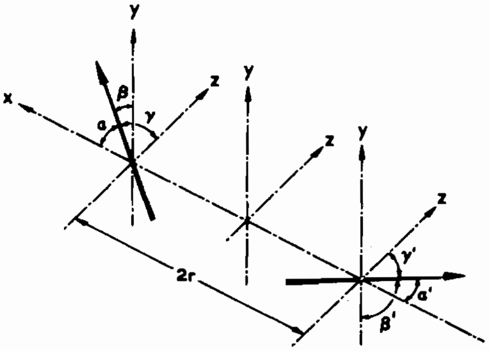

Figure 1. A schematic representation of the transition dipole vectors in one coupling mode. The angles α, β and γ refer to the inclination of the vector 1 to the local axes x, y and z respectively and the angles α', β' and γ' represent the inclination vector 2 to the local axes-x, -y and z respectively. The x axis goes through the midpoints of the vectors.

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vector 2 (Figure 1). The distance between the centres of the two double bonds is defined as 2r. In the exciton approximation the ground state wave function is written as the simple product $\Psi_o = \chi_1\chi_2$ and the two locally and singly excited functions are thus $\Phi_1 = \chi_1'\chi_2$ and $\Phi_2 = \chi_1\chi_2'$ where 1 and 2 label the chromophores whose ground state wave functions are χ_1 and χ_2 respectively and where the primes refer to excited state functions. The excited state functions Φ_1 and Φ_2 are equivalent and contribute equally to the true stationary excited states of the dimer. Thus, if we assume that the two double bonds are essentially in the same environment and that they overlap to a negligible extent, the total excited state functions for the system are

$$\Psi^- = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2)$$

$$\Psi^+ = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)$$

The total wave functions Ψ^+ and Ψ^- represent the in-phase and out-of-phase combinations of the transition dipole moments. In a pictorial sense if we define the Ψ^+ coupling mode as the arrangement of the transition dipole vectors shown in Figure 1, the Ψ^- coupling is represented by reversing the direction of vector 2. In general these two coupling modes will occur at different energies and the corresponding eigen values are

$$\Psi^+;\quad E^+ = \Delta E + V_{12}$$

$$\Psi^-;\quad E^- = \Delta E - V_{12}$$

where ΔE is the transition energy of the isolated $\pi \rightarrow \pi^*$ transition of one double bond and where V_{12} is the multipole interaction energy between the transition dipole moments of the two chromophores. (The static multipole moment interaction difference between the ground and excited states has been set to zero).

For the particular absolute disposition of the double bonds shown in Figure 1, the exciton rotational strength, R^+, for the transition $\Psi_o \rightarrow \Psi^+$ is given by

$$R^+ = +\pi\nu r\rho^2(\cos\gamma\cos\beta' + \cos\beta\cos\gamma')$$

and for the $\Psi_o \rightarrow \Psi^-$ transition the associated rotation strength, R^-, is

$$R^- = -\pi\nu r\rho^2(\cos\gamma\cos\beta' + \cos\beta\cos\gamma')$$

In these expressions ρ is the transition dipole moment of the $\pi \rightarrow \pi^*$ transition which occurs at a wave number frequency of ν and r is the half distance between the centres of the two double bonds. Using the initial choice of phases shown in Figure 1, the interaction between the transition dipole moments is given by

$$V_{12} = \frac{\rho^2}{8r^3}(2\cos\alpha\cos\alpha' - \cos\beta\cos\beta' + \cos\gamma\cos\gamma')$$

This expression was derived using the point-dipole-point-dipole approximation which assumes the transition dipole moments to be point dipoles. Although this approximation may not account quantitatively for the splitting, it will give the correct sense of the splitting which is sufficient for the present purposes.

Thus the exciton theory of optical activity predicts that in the region of the $\pi \rightarrow \pi^*$ transition of *endo*-dicyclopentadiene there should appear two circular dichroism bands of equal intensity but opposite in sign. Furthermore, these two bands should lie symmetrically about the centre of the $\pi \rightarrow \pi^*$ absorption of the isolated chromophore; one band is situated V_{12} to lower energies and the other is displaced V_{12} to higher energies relative to the isolated absorption. Fundamentally circular dichroism is produced by an electronic transition when there is a helical displacement of charge. By definition, a right-handed helical displacement produces positive circular dichroism and a left-handed displacement produces negative circular dichroism. In a pictorial sense we can see how this comes about in the exciton model. It will be seen that in Figure 1, the $\Psi_o \rightarrow \Psi^+$ transition involves a right hand helical displacement whereas the $\Psi_o \rightarrow \Psi^-$ coupling mode engenders a left handed helical displacement of charge. Thus the absolute configuration of any two dissymmetric chromophores follows provided we know the circular dichroism pattern in the relevant region of the spectrum and if we know, at least approximately, the values of the angles defined in Figure 1.

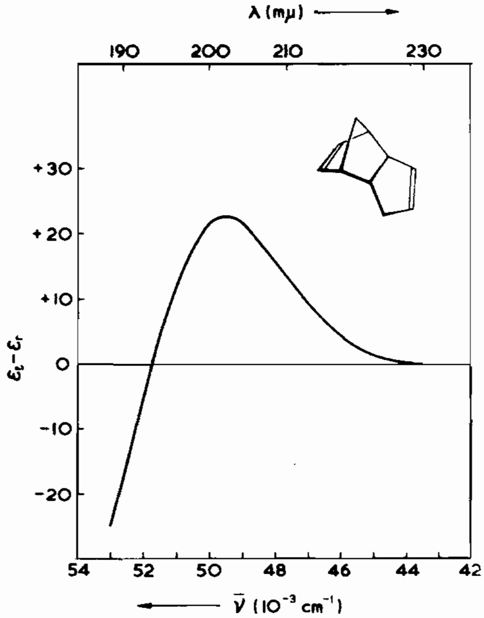

Figure 2. The circular dichroism spectrum of (—)—*endo*—dicyclopentadiene in pentane solution and the predicted absolute configuration.

In Figure 2 we show the circular dichroism of (—) *endo*-dicyclo-pentadiene in heptane solution. Because of the wavelength range of our instrument we were unable to go to energies higher than 53,000 cm^{-1}, but it can be seen that the circular dichroism shows a positive band at 49,500 cm^{-1} and the start of a negative band to higher energies. This is in conformity with the expectations of the exciton theory. The rotational strength of the positive band at 49,500 cm^{-1} is about 0.4×10^{-38} c.g.s. If we take ν for the $\pi \rightarrow \pi^*$ transition of *endo*-dicyclopentadiene as 52,000 cm^{-1} (where the circular dichroism is zero), $\rho = 3.4 \times 10^{-18}$ e.s.u., and $r = 1.55$ Å and using a reasonable choice of angles as suggested by molecular models the calculated exciton rotational strength is about 1×10^{-38} c.g.s. Apart from the errors arising from the use of models to obtain the coordinates of the two double bonds, the discrepancy between the calculated and experimental values of the rotational strengths is at least in part due to the overlap of the two circular dichroism bands similar in energy but opposed in sign. For the particular relationship between the two double bonds in endo-dicyclopentadiene a point-dipole-point-dipole calculation for the two coupling modes shows that the $\Psi_0 \rightarrow \Psi^+$ and $\Psi \rightarrow \Psi^-$ transitions will occur at higher and lower energies respectively. This semi-quantitative result is not critically dependent upon the initial choice of angles provided we assume that *endo*-dicyclopentadiene is a rigid molecule. Therefore, (—) *endo*-dicyclopentadiene has the absolute configuration shown in the inset of Figure 2.

Experimental Section

Optically active *endo*-dicyclopentadiene was prepared by methods described elsewhere[13] and the circular dichroism spectrum was obtained using a Roussel-Jouan Dichrographe (sensitivity 1×10^{-5}).