THE ABSOLUTE CONFIGURATION AND CIRCULAR DICHROISM OF (+)-(1,5)-DIAMINO-TRIPTYCENE*

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Abstract—The absolute configuration of (+)-(1,5)-diamino-triptycene has been determined by calculation of the CD spectrum of the molecule and comparison with the experimental results of Tanaka *et al.*[4] To achieve this the exciton theory of Weigang and Nugent[3] has been extended to include terms representing the retardation of the electro-magnetic wave in the chromophores. The final results of the present study are in contradiction with those of Tanaka *et al.*[4a,b,c]

INTRODUCTION

Measurement of the CD spectrum enables one in principle to determine the absolute configuration of dissymmetric molecules of known conformation.[1] However, in many cases the method fails in practice because of a lack of sufficiently accurate wave-functions, especially for the molecular excited states. In some instances satisfactory results are obtained, e.g. in the case of a symmetric chromophore situated in a dissymmetric environment, resulting in various sector-rules,[2] and, more directly, in cases where exciton theory[3] is applicable. Recently Tanaka *et al*[4] published the results of CD measurements and calculations for some disubstituted triptycenes. The conclusions of that work appeared to be in disagreement with the results obtained by X-ray analysis according to the Bijvoet method. This situation gave rise to the present study of the CD of (+)-(1,5)-diamino-triptycene.

THEORY

The quantities relevant for the calculation of the CD can be found by means of molecular exciton theory.[3] The influence of the central benzene-ring in diamino-triptycene (Fig 1) will be neglected. For symmetry reasons the excited states of this chromophore do not contribute to the CD. There will at most result a certain shift of the energy levels of the two aniline chromophores A and B, which is not expected to affect the sign of the dichroism. So it seems reasonable to describe the CD spectrum in zeroth approximation in terms of the coupled transitions of the two aniline moieties of the molecule. The wave-functions involved in the longest wavelength transitions are given by the exciton theory as linear combinations of products of the energy-eigenfunctions describing the chromo-

phores as isolated systems in the molecule in zeroth approximation.

Indicating by $|A_0)$, $|A_i)$ and $|B_0)$, $|B_i)$ the ground state and the excited state wave-functions of the aniline rings A and B, the ground state of the entire molecule can be written as:

$$\Psi_0 = |A_0 B_0) \tag{1}$$

and the excited states corresponding to excitation of one of the anilines as:

$$\Psi_i^{\pm} = 1/\sqrt{2} \, |A_0 B_i \pm A_i B_0) \tag{2}$$

The wave-functions obey the symmetry of the molecular pointgroup C_2, so that $\hat{C}_2|A_0) = |B_0)$ and $\hat{C}_2|A_i) = |B_i)$. The first order shifts in the energy for states $\Psi_i^{\pm}$ are:

$$\Delta E_i^{\pm} = (A_0 B_i|H'|A_0 B_i) \pm (A_0 B_i|H'|A_i B_0) \tag{3}$$

where H' represents the interaction between the chromophores A and B. When the interaction is restricted to the dipole-dipole term it can be verified that for the lowest two transitions in aniline, which are polarized along the local y-axes (Fig 1), the second term in Eq (3) is positive, so that in both cases $E_i^- < E_i^+$, i.e. the lower energy component of the split bands corresponds to the transition $\Psi_0 \rightarrow \Psi_i^-$. The rotatory strength of a pair of transitions $\Psi_0 \rightarrow \Psi_i^{\pm}$ is calculated with respect to the point 0, the middle of the line connecting the centres of the 6-membered rings A and B. The independency of the rotatory strength from the choice of the origin 0 has been discussed by Weigang *et al.*[3] In the present approximation it is sufficiently warranted.

The electric transition moment is:

$$\vec{m}_{0i}^{\pm} = (\Psi_0|\vec{m}|\Psi_i^{\pm}) = 1/\sqrt{2}\{(B_0|\vec{m}|B_i) \\ \pm (A_0|\vec{m}|A_i)\} = 1/\sqrt{2}\{\vec{m}(B)_{0i} \pm \vec{m}(A)_{0i}\} \tag{4}$$
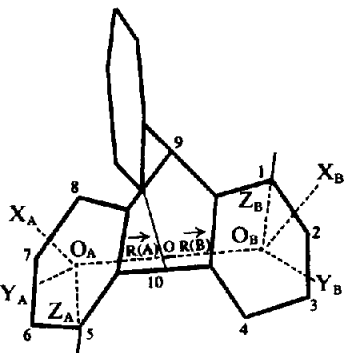

Fig 1.   (+)-(1,5)-Diamino-triptycene.

where $\vec{m}$, $\vec{m}(A)$ and $\vec{m}(B)$ are the electric moment operators for electrons in the entire molecule and in the chromophores A and B, respectively. The magnetic moment operator, which is dependent on the choice of the origin, is formulated as:

$$\vec{\mu} = \frac{e}{2mc}\{\vec{R}(A)\times\vec{p}(A)+\vec{R}(B)\times\vec{p}(B)\}$$

$$+\vec{\mu}(A)+\vec{\mu}(B) \qquad (5)$$

where $\vec{R}(A)$ and $\vec{R}(B)$ are the vectors pointing from 0 to the centres 0_A and 0_B of the rings A and B; $\vec{p}(A)$ and $\vec{p}(B)$ are the total linear momenta of the electrons belonging to A and B and $\vec{\mu}(A)$ and $\vec{\mu}(B)$ are the magnetic moment operators of the two chromophores calculated with respect to the local origins 0_A and 0_B. The magnetic transition moment is now:

$$\vec{\mu}_{i0}^{\pm} = (\Psi_i^{\pm}|\vec{\mu}|\Psi_0) = 1/\sqrt{2}\left\{\frac{e}{2mc}\right.$$

$$\times [\vec{R}(B)\times\vec{p}(B)_{0i}\pm\vec{R}(A)\times\vec{p}(A)_{0i}]$$

$$\left.+\vec{\mu}(B)_{i0}\pm\vec{\mu}(A)_{i0}\right\} \qquad (6)$$

or, using the relation

$$\vec{p}_{i0} = i\frac{2\pi mc\bar{\nu}_{i0}}{e}\vec{m}_{i0} \qquad (7)$$

(which, strictly speaking, is only valid for exact wave-functions):

$$\vec{\mu}_{i0}^{\pm}=1/\sqrt{2}\{i\pi\bar{\nu}_{i0}[\vec{R}(B)\times\vec{m}(B)_{i0}$$

$$\pm\vec{R}(A)\times\vec{m}(A)_{i0}]+\vec{\mu}(B)_{i0}\pm\vec{\mu}(A)_{i0}\} \quad (8)$$

where $\bar{\nu}_{i0} = 1/hc\,(E_i-E_0)$ is the wave-number of the transitions in the isolated chromophores. The rotatory strength of the transition pair is now given by:

$$R_{i0}^{\pm} = Im\,\vec{m}_{0i}^{\pm}\cdot\vec{\mu}_{i0}^{\pm} = Im\,\tfrac{1}{2}\{\pm i\pi\bar{\nu}_{i0}$$

$$\times[\vec{m}(A)_{0i}\cdot\vec{R}(B)\times\vec{m}(B)_{i0}+\vec{m}(B)_{0i}\cdot\vec{R}(A)$$

$$\times\vec{m}(A)_{i0}]\pm\vec{m}(A)_{0i}\cdot\vec{\mu}(B)_{i0}\pm\vec{m}(B)_{0i}\cdot\vec{\mu}(A)_{i0}$$

$$+\vec{m}(A)_{0i}\cdot\vec{\mu}(A)_{i0}+\vec{m}(B)_{0i}\cdot\vec{\mu}(B)_{i0}\} \qquad (9)$$

where the last two terms can be neglected in the present approximation. The unperturbed chromophores are optically inactive. Moreover, in the two pertinent transitions in aniline the electric transition moments are polarized along the local y-axes, so that for these transitions the scalar triple products in Eq (9) vanish, the three vectors lying in one plane. Under these circumstances the rotatory strength can simply be written as:

$$R_{0i}^{\pm} = \pm\tfrac{1}{2}Im\{\vec{m}(A)_{0i}\cdot\vec{\mu}(B)_{i0}+\vec{m}(B)_{0i}\cdot\vec{\mu}(A)_{i0}\}$$

$$\qquad (10)$$

or, for real wave-functions using the relation $\vec{\mu}_{i0} = -\vec{\mu}_{0i}$:

$$R_{0i}^{\pm} = \pm\tfrac{1}{2}i\,(\vec{m}(A)_{0i}\cdot\vec{\mu}(B)_{0i}+\vec{m}(B)_{0i}\cdot\vec{\mu}(A)_{0i}\} \quad (11)$$

It is stated (Tanaka *et al.*[4]), that the displacement of the electric transition moment in one or both chromophores determines the chirality of the molecule. However, from the above arguments it may be shown that the rotatory strength is invariant for such displacements. These may be described by a shift of the local origins in chromophores A and B. If 0_A is shifted over a distance $\vec{a}$ to the point $0'_A$, we can define a new vector $\vec{R}(A)'$ and a new magnetic moment operator $\vec{\mu}(A)'$ taken with respect to this new origin $0'_A$, satisfying the relations:

$$\vec{R}(A) = \vec{R}(A)'-\vec{a} \qquad (12)$$

$$\vec{\mu}(A) = \vec{\mu}(A)'+\frac{e}{2mc}[\vec{a}\times\vec{p}(A)] \qquad (13)$$

Analogous relations hold for a shift $\vec{b}$ of the origin 0_B towards $0'_B$ in ring B. Now the second and fourth terms in Eq (9) can be written as:

$$i\pi\bar{\nu}_{i0}\,\vec{m}(B)_{0i}\cdot\vec{R}(A)\times\vec{m}(A)_{i0}$$

$$= i\pi\bar{\nu}_{i0}\,[\vec{m}(B)_{0i}\cdot\vec{R}(A)'\times\vec{m}(A)_{i0}-\vec{m}(B)_{0i}\cdot\vec{a}$$

$$\times\vec{m}(A)_{i0}] \qquad (14)$$

and

$$\vec{m}(B)_{0i}\cdot\vec{\mu}(A)_{i0} = \vec{m}(B)_{0i}\cdot\vec{\mu}(A)'_{i0}$$

$$+\frac{e}{2mc}\vec{m}(B)_{0i}\cdot\vec{a}\times\vec{p}(A)_{i0} \quad (14')$$

Comparison of the two expressions shows that the two terms in $\vec{a}$ cancel each other in virtue of rela-

tion (7). The same holds true for terms in $\vec{b}$. The rotatory strength can now be formulated as:

$$R_{0i}^{\pm} = \pm\tfrac{1}{2}Im\{i\pi\bar{\nu}_{i0}[\vec{m}(B)_{0i} \cdot \vec{R}(A)' \times \vec{m}(A)_{i0}$$
$$+ \vec{m}(A)_{0i} \cdot \vec{R}(B)' \times \vec{m}(B)_{i0}] + \vec{m}(A)_{0i} \cdot \vec{\mu}(B)'_{i0}$$
$$+ \vec{m}(B)_{0i} \cdot \vec{\mu}(A)'_{i0}\} \tag{15}$$

where the magnetic moments are to be calculated with respect to the new origins. The shifts $\vec{a}$ and $\vec{b}$ can be chosen in such a way that the last two terms in Eq (15) vanish completely. It is evident from Eq (14') that $\vec{a}$ and $\vec{b}$ must then satisfy the conditions:

$$i\vec{\mu}(A)_{0i} = \pi\vec{\nu}_{i0}\,\vec{a} \times \vec{m}(A)_{0i} \quad \text{and} \quad i\vec{\mu}(B)_{0i}$$
$$= \pi\vec{\nu}_{i0}\,\vec{b} \times \vec{m}(B)_{0i} \tag{16}$$

which are formulated for real wave-functions, using relation (7). The rotatory strength then reads:

$$R_{0i}^{\pm} = \pm\pi\bar{\nu}_{i0}[\vec{R}(A)' - \vec{R}(B)'] \cdot \vec{m}(A)_{0i} \times \vec{m}(B)_{0i} \tag{17}$$

The shifts $\vec{a}$ and $\vec{b}$ can only be calculated when both the electric and the magnetic transition moments are known. In that case it seems more simple to use Eq (10) directly.

Application to (+)-(1,5)-diamino-triptycene

The aniline molecule has C_{2v} symmetry and the only transitions which enter the calculation under the present approximation are transitions between $^1A_1$ ground state and $^1B_2$ excited states. These transitions are polarized along the y-axis (Fig 1) and they are accompanied by a magnetic transition moment directed along the x-axis. To calculate the quantities in Eq (11) we used the CI SCF wave-functions from the work by Fischer-Hjalmars.[5] There are two different $^1B_2$ excited states in aniline in the studied spectral region and for both we calculated the electric and the magnetic transition moments. In the calculation of the electric transition moment we only retained contributions of matrix elements where both atomic orbitals were on the same centre and for the magnetic transition moment we only retained contributions of elements where the atomic orbitals were on nearest neighbour centres. Here we used expressions for the matrix elements of the angular momentum operator as given by various authors.[6,7] The results of this calculation are summarized in Table 1. Both transitions in diamino-triptycene corresponding to these transitions in aniline are split according to exciton theory: the longest wave-length component of the band pair corresponds to the transition $\Psi_0 \to \Psi_{\bar{1}}$, so that in Eq (11) the minus sign has to be used for it. The accompanying electric and magnetic transition moments are depicted in Fig 2

Table 1.

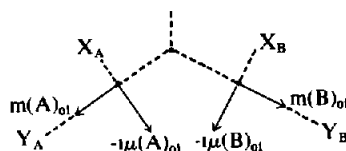| Aniline	Transition moments		
Transition	Energy (eV)	Electric c.g.s. units $\times 10^{18}$	Magnetic, $i\mu_{0i}$ c.g.s. units $\times 10^{21}$
$^1A_1 \to {}^1B_2$	4·699	0·868	0·9537
$^1A_1 \to {}^1B_2$	6·503	5·075	0·9985

Fig 2. Transition moments for the transition $\Psi_0 \to \Psi_{\bar{1}}$ in (+)-(1,5)-diamino-triptycene.

where the signs of the transition moments are taken from Table 1. It is evident from Fig 2 and Eq (11) that the longest wave-length components in both band pairs should have a positive rotatory strength. The short wave-length components then get the opposite sign. The calculated rotatory strengths are summarized in Table 2.

Table 2
(+)-(1,5)-*Diamino-triptycene*

Transition cm^{-1}	Rotatory strength	
	Calculated Biot units	Experimental* Biot units
$35000 - \Delta$	+ 8·28	+12
$35000 + \Delta$	− 8·28	
$45000 - \Delta$	+50·67	+75
$45000 + \Delta$	−50·67	

*From the experimental results of Tanaka *et al.*[4]

CONCLUSION

The experimental CD results of Tanaka *et al*[4] for (+)-(1,5)-diamino-triptycene show a positive-negative pair of CD bands at about 35000 cm^{-1} and a stronger band pair at about 45000 cm^{-1}, the positive component in both cases lying at the lower energy side of the spectrum. Experimental rotatory strengths for these bands may be inferred from these data and they are shown in Table 2. From the results of Table 2 it is evident that within the limits of the approximations used the CD spectrum of Tanaka *et al* corresponds to the absolute configuration depicted in Fig 1, which is the antipode of the configuration given in Ref 4. So there is no disagreement with the results of the X-ray analysis according to the Bijvoet method. It can now be seen how Tanaka *et al* came to the antipodal configuration. They virtually based their conclusions on Eq (17)

for the rotatory strength. Their choice for the direction of shift for the local origins (i.e. towards the NH_2-substituents) was based on the localization of the electric transition moment in the "weighted mean of the transition density".[4] However, the electric transition moment is not localized in the molecule, it is independent of the choice for an origin of the coordinate system. The position of the vectors $\vec{R}(A)'$ and $\vec{R}(B)'$ can only be found according to relation (16) from the sign and magnitude of both the electric and magnetic transition moments. From Table 1 it is seen that in both transition pairs the electric transition moment is directed along the positive y-axis, while the magnetic transition moment, $i\vec{\mu}_{0f}$, is directed along the positive x-axis. Then Eq. (16) implies that $\vec{a}$ and $\vec{b}$ are directed along the negative z-axis (i.e. the origin is shifted away from the NH_2-substituents). So the choice by Tanaka *et al* for the direction of the shift is contradicted by the treatment given above. This obviously leads to the opposite sign for the rotatory strengths.

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