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# Unidimensional Model for Optical Rotatory Power

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A few years ago Tinoco and Woody [1] used a free electron model to evaluate the optical rotatory power of some molecules. Their model is the simplest way to describe the optical activity exactly by a quantumechanical procedure. Such a model is expected to yield reasonable results for a $\pi$ conjugated system arranged according to an approximate helix. Unfortunately very few experimental results are available for molecules which display the above mentioned systems. Tinoco and Woody [1] had not at hand any other example available except the hexahelicene molecule which is not an ideal test case.

Recently Weiss et al. [2] have reported some data about some compounds of the classes of diterpenoids and steroids which contain *cis* $\pi$ conjugated systems in a distorted configuration. A typical example, the lumisterol$_3$, shown in Fig. 1, has the atoms [5, 6, 7, 8] arranged according to a right handed helix.

These compounds afford a suitable example, although of limited applicability, of the model proposed by Tinoco. The optical rotatory power of this last compound has been calculated by Hückel method [3] in the range where the strongest anomalous dispersion for the recorded spectrum is encountered. The most crude approximations made in this calculation involve the matrix elements of rotational strength $R_i$. In addition the experimental transition frequencies employed in the modified Rosenfeld equation,

$$[M] = G \sum_i \frac{R_i \nu^2(\nu_i^2 - \nu^2)}{(\nu_i^2 - \nu^2)^2 + \gamma_i^2 \nu^2} ; \qquad (I)$$

which gives the rotatory dispersion $[M]$ are the experimental ones. In the above equation $\gamma_i$ indicates the dumping factor assumed equal to the experimental half band width. $G$ is an appropriate constant for the used units.

The model proposed by Tinoco [1] could be applied directly to these molecules, but the limited number of atoms which contribute to the $\pi$ system weakens the validity of the free electron model.

The simplest way to improve the model to handle these systems is the introduction of a periodic potential with minima at the nuclei [4]. Therefore we have considered such a modification in order to evaluate its effect upon the optical rotatory power.

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## Theory

The periodical potential $V$ to which the electron is subjected is

$$V = V_0 \left[ (-1)^n \cos\left(\frac{2\pi\, nl}{L}\right) - 1 \right] \qquad -\frac{L}{2} \leq l \leq \frac{L}{2}$$

$$V = \infty \qquad |\, l \,| > \frac{L}{2} \qquad \text{(II)}$$

where $n$ is the number of atoms of the system whose length is $L$, and $V_0$ is the half of the barrier height. As it may be seen, the infinite barriers occur at the distance $L/2n$ from the terminal atoms.

Therefore if $d$ is the average distance between two adjacent atoms of the system, $L = nd$.

The resulting Schroedinger equation is in principle soluble with techniques analogous to those employed in the case of the Mathieu equation, with the added difficulty of non periodic boundary conditions. From a practical viewpoint these procedures amount to the use of a continued fraction method [*5*] which gives enormous numerical troubles. Thus we decided to use an expansion method employing truncated Fourier series*. The potential (II) which establishes the symmetry of the hamiltonian, allows to separate the symmetric eigenfunction $g(l)$ from the antisymmetric ones $u(l)$.

$$g_i(l) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{j=0} C_{ij} \cos\,(2j+1)\,\frac{l\pi}{L}$$

$$u_i(l) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{j=0} D_{ij} \sin\,(2j+2)\,\frac{l\pi}{L} \; .$$

In addition a basis of sine and cosine functions affords a further separation in independent sets. Each of these set collects terms whose arguments differ only by $\pm 2n$.

The matrix elements of the hamiltonian $H_{JK}$ are

$$H_{JK} = \left[ \tfrac{1}{2} \left(\frac{J\pi}{L}\right)^2 - V_0 \right] \delta(J, K) + \frac{V_0}{2} (-1)^n \cdot q \cdot \delta(J, |\, K - 2n \,|) \; ;$$

where

$$q = +1$$

$$J = 2i + 1 \quad \text{for a } g(l) \text{ function} \qquad (i, j) = 0, 1, 2, 3, \ldots\ldots$$

$$K = 2j + 2$$

$$q = \frac{|\, K - 2n \,|}{K - 2n} \qquad \text{for a } u(l) \text{ function.}$$

Since the solution of the variational problem is reduced to the diagonalization of a finite matrix, the problem of the accuracy of the results arises. After a few trials we found that to achieve a accuracy of six significant figures for the levels involved in all subsequent calculations, about ten terms were needed for each set. It must be noted that at this level the actual geometry does not play any role, while it becomes essential for the calculation of matrix elements of the rotatory strength operator.

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* The calculations was performed by IBM 7090 of CNUCE, Pisa.

The molar rotatory power has been calculated by (I) where the constant $G$ is now given by $G = \frac{48N}{\hbar c}$.

## Results and Discussion

For the lumisterol$_3$ (Fig. 1) the geometrical parameters which define the model are derivable from the crystal structure data [*6*]. The average interatomic distance $d$ is $1.37_8$ Å, the bond angles are assumed all equal to 120° and the dihedral angle to 8.3°. From these quantities it is possible to determine the pitch $2\pi b$ and the radius $a$ of an helix of total length of $4 \times 1.37_8$ Å, whose path almost touches the four atoms. Thus $a = 1.312$ Å, $b = 0.0533$ Å. The number of turns $p$ is obtainable for the relation

$$p = \frac{nd}{2\pi(a^2 + b^2)^{1/2}} .$$

It is perhaps important to note that $b > 0$ means a right handed helix.

The potential barrier $2\,V_0$ is determined so as to reproduce the first experimental transition at 4.57 eV [*2*], and its value turns out to be 39.35 eV. Tab. 1 shows the calculated dipole moment $D$, rotatory and oscillatory strength $R$ resp. $f$ of the first three transitions, which are the only ones giving significant contribution, together with the experimental data [*2*]. The experimental data refer only to two transitions while the theory predicts two transitions very close together, degenerate in the case of the Hückel treatment of CHARNEY [*3*], for the $A \to A$ transitions.

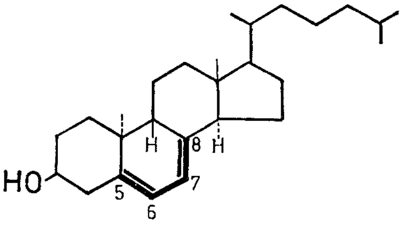

Fig. 1. Lumisterol$_3$

It is not easy to estimate the correctness of the prediction for lack of experimental data; however, it is rather gratifying to note that the experimental rotatory dispersion (R.D.) spectrum, reported in Fig. 2, gives some support to this. The presence of another transition around 190 mμ with a rotatory dispersion

Table 1. *Calculated and observed transitions and calculated dipole, rotational, oscillatory strengths of the lumisterol$_3$*

| Symmetry | $\Delta E$ (eV) calc. | $\Delta E$ (eV) obs. | $D$ $\times 10^{35}$cgs | $R$ $\times 10^{38}$cgs | $f$ |
|---|---|---|---|---|---|
| $A \to B$ | 4.570 | 4.57 | 1.1194 | 0.12525 | 0.1940 |
| $A \to A$ | 7.524 | 6.00 | 0.5534 | −0.02874 | 0.1580 |
| $A \to A$ | 7.724 | | 0.3320 | −0.01549 | 0.0973 |

Table 2. *Calculated and observed transitions and calculated dipole, rotational, oscillatory strengths of the lumisterol$_3$ in the free electron model*

| Symmetry | $\Delta E$ (eV) calc. | $\Delta E$ (eV) obs. | $D$ $\times 10^{35}$cgs | $R$ $\times 10^{38}$cgs | $f$ |
|---|---|---|---|---|---|
| $A \to B$ | 6.188 | 4.57 | 0.1278 | 0.14222 | 0.3000 |
| $A \to A$ | 9.901 | 6.00 | 0.3107 | −0.01493 | 0.1167 |

of same sign as the 207 mμ band* might explain the fact that the (R.D.) spectrum does not change sign in that region. This is why we refer in Tab. 1 the experimental value of 6.00 eV to both the calculated transition $A \to A$.

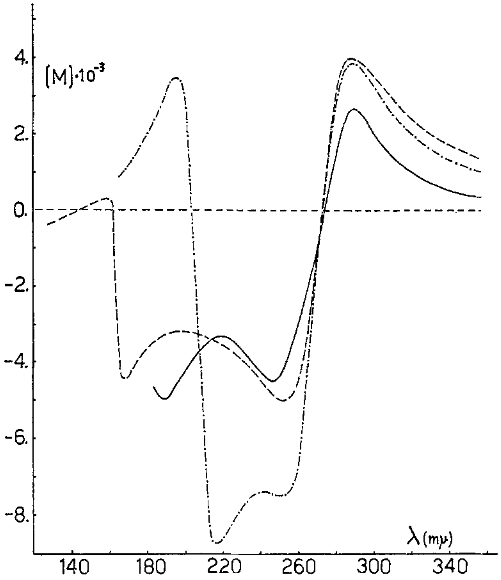

Fig. 2. Rotatory dispersion of the lumisterol$_3$

Fig. 3 reports the calculated one for three values of the dumping factor of the third transition. The dumping factors of the two transitions obtained from experiment** are $\gamma_1 = 0.0143 \cdot 10^{16}$ sec$^{-1}$ (35 mμ); $\gamma_2 = 0.0133 \cdot 10^{16}$ sec$^{-1}$ (19 mμ). For the third one no experimental data are available, but for the wide range of values of $\gamma_3$ tried, which include the correct one, the changes in the spectrum are negligible.

Fig. 4 reports the R.D. spectrum obtained by the use of more crude free electron model, applied to the same geometrical system. Apart the noticeable discrepances between the observed and calculated transitions, reported in Tab. 2, the resulting R.D. spectrum shown in Fig. 4, compares very unfavourably with the experimental one. Thus the introduction of the periodic perturbing potential brings in a substantial improvement of the overall agreement.

It was thought interesting to treat by the present method a three π conjugated system in discorted cis configuration. The geometrical parameters of the resulting

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* This reviewed value of 207 mμ was kindly supplied to us by Dr. Charney.

** Private communication of Dr. Charney.

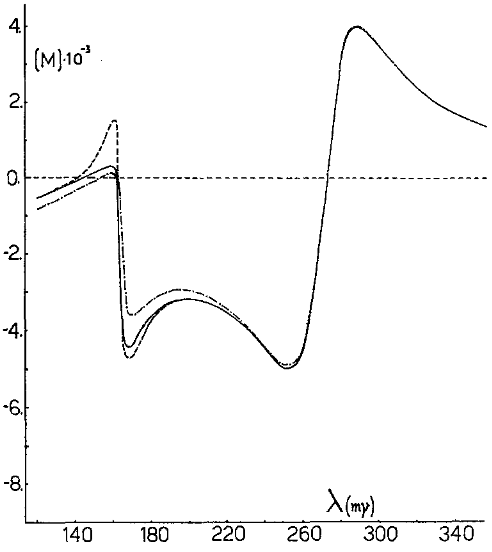

Fig. 3. Calculated rotatory dispersion of the lumisterol$_3$ for different values of the dumping factor of second $A \rightarrow A$ transition

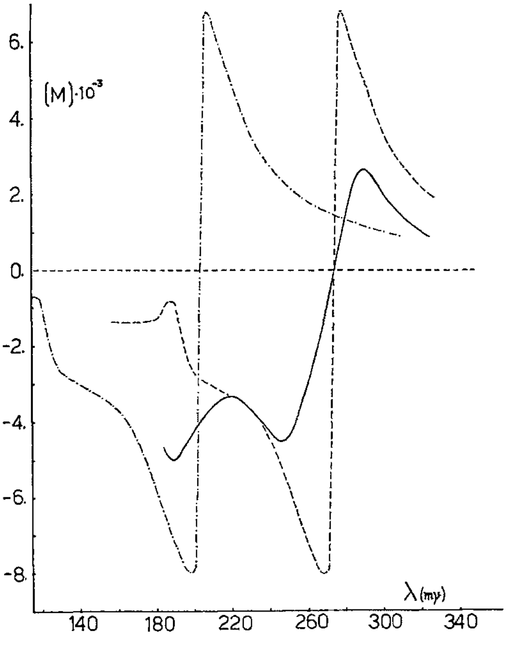

Fig. 4. Rotatory dispersion of the lumisterol$_3$ calculated by the free electron model (F.E.M. curve). The F.E.M. shifted curve represents the F.E.M. curve opportunately displaced in order to facilitate the comparison with the experimental data

Table 3. *Calculated transitions, dipole, rotational, oscillatory strengths of a trienic system arranged in a helix*

| Symmetry | $\Delta E$ (eV) calc. | obs. | $D$ $\times 10^{35}$cgs | $R$ $\times 10^{38}$cgs | $f$ |
|---|---|---|---|---|---|
| $A \to B$ | 2.985 | ? | 0.7292 | 0.15044 | 0.0826 |
| $A \to A$ | 5.304 | ? | 0.9768 | −0.09344 | 0.1965 |
| $A \to A$ | 6.025 | ? | 0.9312 | −0.13424 | 0.2129 |

helix of appropriate length were taken equals to there of lumisterol. Because the pitch could be different from that of lumisterol, we report also two results for two probable values of it. In Tab. 3 the calculated dipole, rotatory, and oscillatory strength are given and Fig. 5 shown the R.D. spectrum for two values of the pitch and for values of $\gamma_1$, $\gamma_2$, $\gamma_3$ equals to those of lumisterol$_3$.

No calculation has been made for the hexahelicene. For this molecule in fact the unidimensional model seems inappropriate because of the ambiguities connected with the selection of suitable geometrical parameters which are of paramount importance. TINOCO et al. [*1*] in their treatment determine the radius of the unidimensional helix by imposing that the first calculated transition is coincident with the experimental one. They considered as first transition that at 31,500 cm$^{-1}$, while another one is reported at 24,000 cm$^{-1}$ [*7*]. This choice might be valid in the case that the 24,000 cm$^{-1}$ transition has negligible rotatory strength, which is not known for lack of the pertinent experimental data [*8*]. Thus it should be a predominantly "radial" transition, which might be accounted for only by a more sophisticated model.

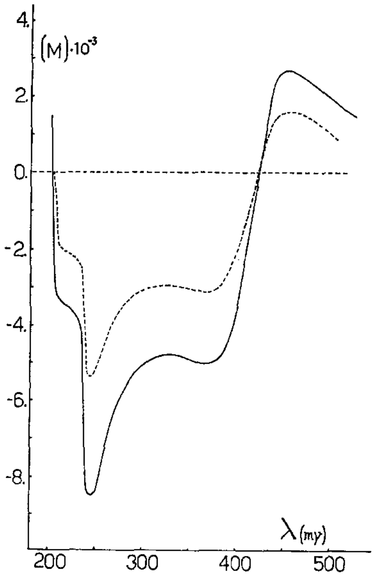

Fig. 5. Calculated rotatory dispersion of a trienic system arranged in a helix for different values of pitch

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