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Chiroptical Properties and Absolute Configuration of Chiral, Open Chain Di- and Tri-substituted Allenes : a Polarizability Approach

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A second order treatment of the optical activity of chiral di- and tri-substituted open chain allenes, by means of the polarizability model of DeVoe, makes it possible to establish a simple relationship between optical rotatory power and absolute configuration of these compounds.

INTRODUCTION

The calculation of circular dichroism (CD) data by means of dynamic coupling procedures[1] (coupled oscillators[1,2] or polarizability[3] models) is increasingly used in organic chemistry to establish spectra-structure relationship and to assign[2] molecular absolute configurations, *i. e.* to solve one of the most difficult problems in structural chemistry. Generally, the above approaches are formulated in a quantum-mechanical frame,[3] even if several procedures are known,[4] like the DeVoe model,[4c,d] 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 sub-systems. This model has been successfully used to reproduce the CD spectra of different multichromophoric systems.[5] A particular effort has been made to treat even simple organic molecules composed of a single chromophore perturbed by alkyl groups only.[6] In this frame one of the applications reported deals[6c] with the calculation of the circular dichroism allied to the $^1A_1 \rightarrow {}^1B_2$ electrically allowed transition in 1,3- disubstituted chiral allenes. This fact stimulated us to reconsider the optical activity of chiral, open chain 1,3-di- and 1,3,3-trisubstituted allenes[7] with the aim of finding a simple relationship between the CD and structure.

RESULTS AND DISCUSSION

The DeVoe Approach

Like any other independent-system procedure,[1,3] the DeVoe treatment of the optical properties of a molecule requires a division of the molecule in a set of subsystems, which have to be suitably characterized. Therefore, each group is represented in terms of one (or more) classical oscillator: each oscillator represents an electric dipole allowed transition, defined by the polarization direction $\vec{e}_i$ and the complex polarizability $\alpha_i(\nu) = R_i(\nu) + i\,I_j(\nu)$. $I_i(\tilde{\nu})$ is obtainable from the experiment, *i. e.* from the absorption spectra of compounds which can be considered good models of the sub-systems, $R_i(\nu)$ can be calculated from $I_i(\tilde{\nu})$ by means of the Kronig-Kramers transforms.[4c,d] Under the external radiation, each sub-unit is polarized depending on the local electric field $\vec{E}$, this field being the incident field plus the fields from polarizations of the other sub-units:

$$m_i(\tilde{\nu}) = \alpha_i(\tilde{\nu}) \text{ (component of the total field along } \vec{e}_i) \tag{1}$$

$$= \alpha_i(\tilde{\nu})\,[\vec{e}_i \cdot \vec{E}_i - \Sigma_{j \neq 1} G_{ij}\, m_j(\tilde{\nu})]$$

where $G_{ij} = \tau_{ij}\,[\vec{e}_i \cdot \vec{e}_j - 3\,(\vec{e}_i \cdot \vec{e}_{ij})\,(\vec{e}_j \cdot \vec{e}_{ij})]$, is the point dipole — point dipole interaction term.

This is 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:

$$m_i(\nu) = \Sigma_j\, A_{ij} \cdot (\vec{e}_j \cdot \vec{E}_j) \tag{2}$$

where **A** is the inverse of matrix **B**, $B_{ij} = \delta_{ij}/\alpha_i + G_{ij}$. It is then possible to calculate vector $\vec{P}$, electric polarization, and the complex refractive indices for left- and right-circularly polarized radiation, obtaining, after completely reliable approximations,[4c,d] the expression for the circular dichroism as:

$$\Delta\,\epsilon\,(\tilde{\nu}) = (24/3298)\,\pi^2\,N\,\tilde{\nu}^2 \sum_{i \geq j} \vec{e}_i \times \vec{e}_j \cdot \vec{R}_{ij}\, ImA_{ij} \tag{3}$$

where ImA_{ij} means the imaginary part of the element A_{ij}.

The DeVoe model is an exact (all-order) treatment because the mutual action of the dipoles, perturbed not only by the external field but also by the presence of the other polarized dipoles, is taken account. This involves the inversion of the matrix **B** at every frequency. This procedure is quite long and a practical calculation requires the use of a computer.

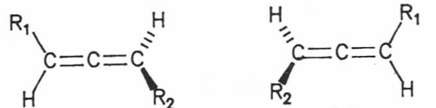
In order to formulate a simple, qualitative correlation between structure and CD properties, we use here the alternative approach of approximating the elements A_{ij} by perturbative methods. This approach presents the further advantage that a physical insight into the origin of optical activity is easily gained. Then:[5f]

$$A_{ij} = \alpha_i(\tilde{\nu}) - \Sigma_j\, \alpha_i(\tilde{\nu})\, G_{ij}\, \alpha_j(\tilde{\nu}) + \Sigma_j\, \Sigma_k\, \alpha_i(\tilde{\nu})\, G_{ij}\, \alpha_j(\tilde{\nu})\, G_{jk}\, \alpha_k(\tilde{\nu}) + \ldots \tag{4}$$

The first term of this series represents the polarization of the unit i due to the external field, the second one the polarization of unit i due to unit j polarized by the external field only (pairwise interactions or first order perturbation, this term gives rise to the so called first order optical activity), the third is the polarization of unit i due to unit j which, in turn, is perturbed by 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 is provided. Therefore, the elements A_{ij} which are necessary to calculate the CD can be quite easily evaluated.

1,3-Disubstituted Allenes

In this section the above approach is applied to systems having structures *1* (Chart 1):



(S) (R)

1a 1b

Chart 1

The CD allied to the allowed $^1A_1 \rightarrow {}^1B_2$ transition of the chromophore could be a suitable spectroscopic probe. Unfortunately, this absorption occurs at about 171 nm and only a few CD data are reported[7e,g,m] in the vacuum UV region. However, as it has been previously pointed out,[c,e] this transition dominates the sign of the rotation at the sodium D line; therefore, it can be used to compare the results of the present analysis with the experimental data. In practice, system *1* will be considered an aggregate of purely electric oscillators, *i. e.* the allene moiety (chromophore) and the C—R bonds (perturbers). Only the polarizability allied to the allene electrically allowed $^1A_1 \rightarrow {}^1B_2$ transition, polarized along the cumulated double bond axis, will be taken into account: hence, on the chromophore will be placed a single oscillator, $\vec{e}_1$, located at the central carbon atom and directed along the C=C=C bond. As far as the description of the substituents is concerned, a single dipole will be placed along each of the =C—R bonds ($\vec{e}_2$, $\vec{e}_3$): this is equivalent to say that each perturber is representable by a single polarizability along the =C—R direction.[6c,7c,7e] To each of the oscillators employed, a frequency dependent complex polaribazility $\alpha_i(\tilde{\nu})$ should be attributed,[5,6] in order to carry out quantitative calculations. In summary, all the parameters necessary to carry out a calculation, are indicated in the chart 2.

For such a system Eq. 3 becomes:

$$\Delta\epsilon(\tilde{\nu}) = 48/3298)\,\pi^2 N \tilde{\nu}^2 \{\vec{e}_1 \times \vec{e}_2 \cdot \vec{R}_{1\,2}\, ImA_{1\,2} + \vec{e}_1\, x \vec{e}_3 \cdot \vec{R}_{1\,3}\, ImA_{1\,3} + \\ + \vec{e}_2\, x \vec{e}_3 \cdot \vec{R}_{2\,3}\, ImA_{2\,3}\} \qquad (5)$$

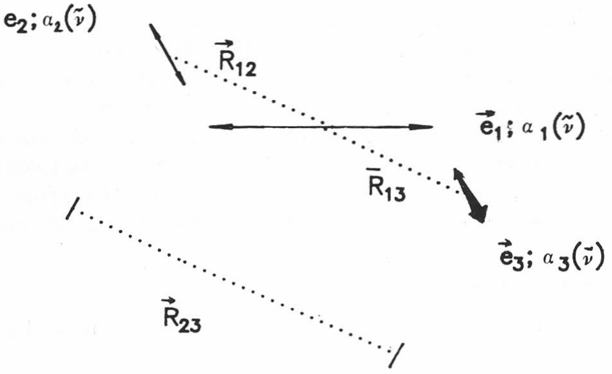


Chart 2

This formula is simplified considering that $\vec{e}_1$, $\vec{e}_2$ and $\vec{e}_1$, $\vec{e}_3$ are coplanar, so that the first two terms of eq. (5) go to zero. Now we evaluate the elements A_{ij} by the perturbative approach previously discussed, limited to the second order terms. Using eq. (4), eq. (5) becomes then:

$$\Delta\epsilon(\tilde{\nu}) = (48/3298)\,\pi^2 N \nu^2\, Im\,\{-\,\alpha_2 G_{23}\alpha_3 + \alpha_2 G_{21}\alpha_1 G_{13}\alpha_3\} \qquad (6)$$

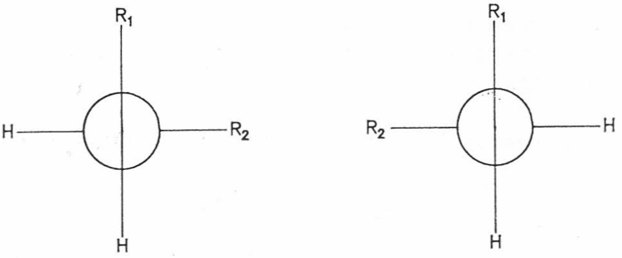
This expression can be further simplified considering that we are interested in $\Delta\varepsilon(\tilde{\nu})$ in the absorption region of the chromophore: assuming[8] that chromophore and perturbes absorb in different frequency regions (*i. e.* their absorption bands do not overlap) we have $I_2 = I_3 = 0$ where $I_1 \neq 0$. Therefore, in the frequency range of the chromophore:

$$Im A_{23} = G_{21} G_{13} I_1(\tilde{\nu}) R_2(\tilde{\nu}) R_3(\tilde{\nu}) \qquad (7)$$

Hence:

$$\Delta\epsilon(\tilde{\nu}) = (48/3298)\,\pi^2 N \tilde{\nu}^2\, \vec{e}_2 \times \vec{e}_3 \cdot \vec{R}_{23} G_{21} G_{13} I_1(\tilde{\nu}) R_2(\tilde{\nu}) R_3(\tilde{\nu}) \qquad (8)$$

Thus, the sum in (5) is reduced to a single term: the sign of the CD is determined by the product of the geometrical factor $\vec{e}_2 x \vec{e}_3 \cdot \vec{R}_{23} G_{21} G_{l3}$, which depends only on the configuration of the compound, with the term $I_1(\tilde{\nu})\, R_2(\tilde{\nu})\, R_3(\tilde{\nu})$, which, in the absorption region of the chromophore, is monosignate independently of the values of the actual polarizabilities. In practice, for the *S* absolute configuration (Chart 3) a positive Cotton effect of the ${}^1A_1 \rightarrow {}^1B_2$ transition is provided. Clearly, a similar result will be obtained for any other chiral allene where the geometrical and polarizability conditions are similar to the above ones. For instance, for the (*R*)-halogenoallenes (Chart 3, $R_1 = Bu^t$, $R_2 = Cl$, Br I) a negative value of the CD is predicted, and a strong negative Cotton effect is actually measured.[7m] The simple rule represented in Chart 3 gives the required qualitative spectrum-structure relationship.



(S) (R)

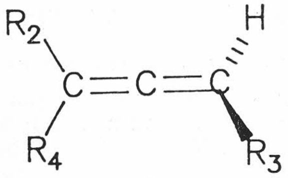
positive c·d· negative c·d·

Chart 3

From a numerical point of view eq. (8) gives, for (*S*)-1,3-dimethylallene, $\Delta\varepsilon_{\max} = +1.05$, which is in practice coincident with the all-order value (+0.96), showing that eq. (8) essentially contains all the physics necessary to understand the dynamic origin of the CD allene $^1A_1 \rightarrow {}^1B_2$ transition. In practice, we have only incomplete experimental CD and optical rotatory power data to make comparisons with the numerical results obtained from eq. (8) by means of reasonable polarizability values.[6c] However, from the $\Delta\varepsilon$ values a rotational strength can be computed from which, applying the Drude equation, molar rotatory powers can be evaluated: this calculation, in the case of (*S*)-1,3-dimethylalene, affords $[M]_D$ of about +50, to be compared with the experimental value[7c] of +59. In the same way, for (S)-1,3-di-tertbutylallene, a molar rotatory power can be obtained of +207, whilst the experimental value[7c] is +188. The higher value calculated for the latter is larger than that of the former: this is a consequence of the higher polarizability allied to the Bu^t with respect to that related to the Me group.

1,3,3-Trisubstituted Allenes

The above second order treatment can be easily extended to trisubstituted systems by taking into account one more oscillator to describe the polarizability of the additional bond =C—R$_4$ in structure *2* (Chart 4):



2

Chart 4

The problem to be solved in the present case concerns an aggregate of four oscillators (the chromophore and three perturbers) which interact. Such a treatment provides then:

$$\Delta\epsilon(\tilde{\nu}) = (48/3298)\,\pi^2 N \tilde{\nu}^2 \{\vec{e}_2 \times \vec{e}_3 \cdot \vec{R}_{2\,3}\, G_{2\,1}\, G_{1\,3}\, I_1(\tilde{\nu})\, R_2 \overset{\rightarrow}{(\nu)}\, R_3 \overset{\rightarrow}{(\nu)} +$$

$$+ \vec{e}_3 \times \vec{e}_4 \cdot \vec{R}_{3\,4}\, G_{3\,1}\, G_{1\,4}\, I_1(\tilde{\nu})\, R_3(\tilde{\nu})\, R_4(\tilde{\nu})\}$$

In practice, this formula says that a system like *2* is equivalent to what is reported in Chart 5:

Chart 5

i. e., the CD results from two structures of opposite chirality. Since the geometrical factors have the same aboslute value, the sign of the CD will depend on the following relationship:

$$R_2(\tilde{\nu}) \gtrless R_4(\tilde{\nu})$$

This is equivalent to saying that *2* (Chart 4) will give a positive CD if $R_2(\tilde{\nu}) > R_4(\tilde{\nu})$, *i. e.* if group R_2 is more polarizable than R_4, and a negative value in the opposite case. This provides a polarizability formulation of the Lowe-Brewster[7a,b] rule. The most significant consequence of these results concerns the absolute configuration of two halogenoallenes, *i. e.* (+)-1-chloro-3,4,4-trimethyl-1,2-pentadiene and (+)-1-bromo-3,4,4-trimethyl-1,2-pentadiene. Following the present rule, with the reasonable assumption that the Bu^t group is more polarizable than the Me one, as discussed in the previous section, the same *S* absolute configuration can be assigned to the dextrorotatory chloro and bromo derivatives. This result is in agreement with a recent reassignment[10] of the absolute configuration of (—)-3,4,4-trimethyl-1-pentyn-3-ol, from which the above halogenoallenes have been prepared.[11] It is certainly interesting to note, in this respect, that, in the original formulation[7a] of the Lowe-Brewster rule, since the (*R*) configuration was erroneously attributed to the (+)-chloro derivative, one had to consider the Bu^t less polarizable than the methyl, to provide homogeneous results.

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8. Considering that the electrically allowed $^1A_1 \rightarrow {}^1B_2$ transition of the allene chromophore occurs at about 171 nm, this assumption can be considered certainly valid in the case of purely alkyl perturbers (hydrocarbons begin[9] to absorb strongly at wavelengths shorter than 150 nm). Furthermore, simple chromophores (such as alcohols, amines and alkyl chlorides) show[9] only weak absorption bands down to 155—160 nm; therefore, at least for derivatives containing this kind of cromophores, this assumption can be considered valid.

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SAŽETAK

Kiroptička svojstva i apsolutna konfiguracija kiralnih, ravnolančanih, di- i tri-supstituiranih alena: pristup putem polarizabilnosti

Carlo Rosini, Maurizio Zandomeneghi i Piero Salvadori

Obradba »drugog stupnja« optičke aktivnosti kiralnih di- i tri-supstituiranih alena, koristeći DeVoeov model polarizabilnosti, omogućila je da se utvrdi jednostavan odnos između optičke rotacijske snage i apsolutne konfiguracije tih spojeva.