sine to be 2*R*,3*R*,4*R*,5*R* as previously proposed.[3f]

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Supplementary Material Available: Experimental procedures, spectral data, and physical properties for compounds **6–8** (R^1 = Ph, R^2 = H), **10–11** (R^1 = 3,4-$(MeO)_2C_6H_3$), **13**, **15–20**, and **4a** and an X-ray ORTEP drawing and crystallographic parameters for **4a** (8 pages). Ordering information is given on any current masthead page.

Articles

About the Origin of the Chiroptical Properties of the Planar Diene Chromophore in Cyclohexylidenepropene Derivatives[†]

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The circular dichroism of the lowest energy $\pi-\pi^*$ transition in cyclohexylidenepropenes (a class of s-trans dienes) has been investigated theoretically. Two calculation methods, viz. the De Voe coupled oscillators theory and a semiempirical MO–SCF method (CNDO/S), have been employed. CD signs opposite to those experimentally found by Walborsky and co-workers have been obtained for every molecule studied. A possible origin of this disagreement cannot be found in a twist of the diene chromophore on the basis of the theoretical conformational analysis (MMP2 and ab initio SCF calculations give planar diene structure); the origin of the optical activity of these compounds seems then to be an open question.

Introduction

The origin of optical activity in the diene chromophore, in particular the circular dichroism (cd) of the lowest energy $\pi-\pi^*$ transition, has been the subject of several experimental and theoretical investigations,[1] and various chirality rules have been proposed[1] to correlate the spectral data with the molecular structure. Most of the interest has been devoted[1] to 1,3-cisoid dienes, while the transoid systems received much less attention. Only in recent years have some interesting papers by Walborsky and co-workers appeared in the literature[2-4] dealing with the synthesis, structure, and chiroptical properties of cyclohexylidene-substituted, planar s-trans butadienes. It is worth mentioning that they proposed[2] a sector rule, the planar diene rule, to correlate the sign of the long-wavelength $\pi-\pi^*$ cd transition with the absolute configuration. They also provided a qualitative interpretation[3] of the cd data of these systems on the basis of the two-group electric dipole mechanism.[5] In 1988, Walborsky, Reddy, and Brewster empirically introduced[6] a more complex sector rule, which explicitly superseded the first one. In addition, they also attempted, without success, to apply the Weigang treatment[7] to have quantitative estimation of the cd allied to lowest energy $\pi \rightarrow \pi^*$ transition of these systems. In this paper, we try to provide a *quantitative* analysis of the cd data of the previous transoid dienes employing a dynamic coupling method of calculation, the De Voe model,[8] which has been successfully used in several instances to reproduce the cd of simple symmetric chromophores perturbed by polarizable groups dissymmetrically disposed around it. This model has been described in detail elsewhere,[9] so only most important features will be presented here. A De Voe treatment of the optical properties of a chiral molecule requires a division of the molecule in a set of suitable

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[†] This paper is dedicated to the memory of Prof. Piero Pino (1921–1989).

[‡] Scuola Normale Superiore.

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(1) Taking into account the large body of papers that appeared about the chiroptical properties of the diene chromophore, we only quote here those references where a general discussion of the previous literature is also reported: (a) Charney, E. *The molecule basis of optical activity: Optical Rotatory Dispersion and Circular Dichroism*; Wiley: New york, 1979. (b) Lightner, D. A.; Boumann, T. D.; Gawronsky, J. K.; Gawronska, K.; Clappuis, J. L.; Gast, B. V.; Hansen, A. T. *J. Am. Chem. Soc.* **1981**, *103*, 5314. (c) Brown, A. R.: Drake, A. F.; Kearney, F. R.; Mason, S. F.; Paquette, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 6123.

(2) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3264. Actually, these authors also treated other cyclohexylidene-substituted systems, such as unsaturated aldehydes, ketones, and esters.

(3) Gawronsky, J. K.; Walborsky, H. M. *J. Org. Chem.* **1986**, *108*, 2863.

(4) (a) Walborsky, H. M.; Gawronska, K.; Gawronsky, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 6719. (b) Gawronsky, J. K.; Reddy, S. M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6726.

(5) See, for instance: Mason, S. F. *Molecular Optical Activity and the Chiral Discrimination*; Cambridge University Press: Cambridge, 1982; p 42 and references therein.

(6) Walborsky, H. M.; Madhava Reddy, S.; Brewster, J. H. *J. Org. Chem.* **1988**, *53*, 4832.

(7) Weigang, O. E. *J. Am. Chem. Soc.* **1979**, *101*, 1965.

(8) De Voe, H. *J. Chem. Phys.* **1965**, *43*, 3199.

(9) (a) Zandomeneghi, M.; Rosini, C.; Salvadori, P. *Chem. Phys. Lett.* **1976**, *44*, 533. (b) Rosini, C.; Zandomeneghi, M.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1978**, 877. (c) Zandomeneghi, M. *J. Phys. Chem.* **1979**, *83*, 2969. (d) Salvadori, P.; Bertucci, C.; Rosini, C.; Zandomeneghi, M.; Gallo, G. G.; Martinelli, E.; Ferrari, P. *J. Am. Chem. Soc.* **1981**, *103*, 5553. (e) Rosini, C.; Zandomeneghi, M. *Gazz. Chim. Ital.* **1981**, *111*, 493. (f) Zandomeneghi, M.; Rosini, C.; Drake, A. F. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 567. (g) Rosini, C.; Giacomelli, G.; Salvadori, P. *J. Org. Chem.* **1984**, *49*, 3394. (h) Rosini, C.; Bertucci, C.; Salvadori, P.; Zandomeneghi, M. *J. Am. Chem. Soc.* **1985**, *107*, 17.

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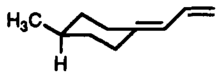
subsystems (the chromophore and the perturbers that make it dissymmetric): they are polarized by the external electromagnetic field and are coupled by their own local fields. The optical properties (absorption, refraction, optical rotation, and circular dichroism) can be calculated taking into account the previous interaction among the subsystems.

Results

In order to quantitatively reproduce the cd data of the diene chromophore in cyclohexylidene derivatires, we shall use as reference compound



1, (αR)-(+)-(4-methylcyclohexylidene)propene
ε_{max} = 24 300 (237.5 nm), $\Delta\varepsilon$ = +3.73

The s-trans butadiene chromophore belongs to the point group C_{2h}, and the lowest $\pi-\pi^*$ transition has been assigned to the electric dipole allowed $^1Ag-^1Bu$ transition.[10] Compound **1** is quite well characterized[2] from a structural point of view (in fact, its absolute configuration has been confidently assigned by Walborsky,[11] while by means of molecular mechanics calculations it has been established that the butadiene moiety is in a s-trans planar situation; furthermore, the conformer with the equatorial methyl group is in practice the only one (~95%) present in solution at room temperature.

Given this information, the geometry of the minimum-energy conformer has been used in the De Voe calculations.

The interacting subsystems in which **1** can be separated are the trans diene chromophore and its aliphatic environment. The low-energy $\pi'-\pi^*$ (^1Ag-Bu) transition (ϵ_{max} of about 25 000 in trans butadiene) is in-plane polarized and directed along the C1–C4 carbon of the diene function. Therefore, it has been represented, in our calculations, as a single dipole oriented as previously said; it was given a dipolar strength of about 36 D^2 centered at 42 000 cm^{-1} in order to reproduce the absorption data.

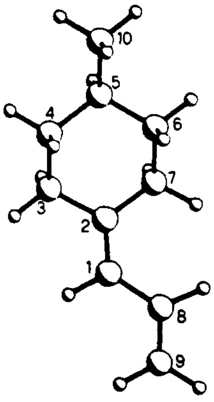
Calculations have been carried out allowing the chromophore to interact with all the C–C and C–H bonds of the molecule. Afterwards, we considered every pairwise interaction between the chromophore and each C–C or C–H bond separately in order to gain information about the contribution of each single perturber.

For C–C bonds, we initially used the parameterization already employed in previous works,[9e] i.e., on each carbon atom we located a single oscillator directed along the bond and it was given a dipolar strength of 2.0 D^2 at 75.0 kK.

In this way, we obtained a negative value of ϵ for the $^1Ag-^1Bu$ transition. Successively, to improve the polarizability parametrization, we located three dipoles on each carbon atom, the first one directed along the bond and the other two normal to it. These three dipoles can be considered as the diagonal elements of the polarizability tensor; their values were chosen as to take into account the polarizability anisotropy of the bonds. For C–C bonds having a rather strong anisotropy, we used values of dipolar strength of 2.5 D^2 for α_{xx} ($\alpha^{\parallel}$) and 0.8 D^2 for α_{yy} and α_{zz} ($\alpha^{\perp}$).[12]

A similar parametrization was used to describe the C–H bonds, the only difference being that dipolar strengths of 1.2 D^2 for $\alpha^{\parallel}$ and 0.8 D^2 for $\alpha^{\perp}$ (centered at 100 kK) were used, according to the fundamental work of Raymonda and Sympson.[13]

Table I. Contribution of Various Bonds to Optical Activity



(αR)-(+)-(4-methylcyclohexylidene)propene

atoms	$\Delta\epsilon$	atoms	$\Delta\epsilon$
C3–C4	+1.2	C3–H_{ax}	–0.22
C7–C6	–1.59	C4–H_{ax}	0.0
C4–C5	+0.08	C4–H_{eq}	0.0
C6–C5	–0.13	C6–H_{ax}	+0.01
C5–C10	–0.31	C6–H_{eq}	0.0
C7–H_{ax}	+0.47	C5–H_{ax}	+0.03

With the previous geometrical and spectroscopic parameters, De Voe calculations of cd have been carried out. The results are reported in Table I, where one can also see the theoretical cd value corresponding to each bond.

The most relevant aspects of these calculations can be summarized as follows:

(a) Each bond provides its own contribution (in sign and intensity) depending on the polarizability and on its distance and orientation with respect to the chromophore. Among the C–C perturbers the strongest contributions are provided by the C3–C4 and C6–C7 bonds, i.e., the nearest ones to the chromophore that are not coplanar to it.

(b) The previous two bonds give rise to oppositely signed contribution to the $\pi-\pi^*$ cd. In fact, the cd deriving from the coupling of two different transitions (oscillators) is given by[9a,b] the following:

$$\Delta\epsilon = (48/3296)\pi^2 N\tilde{\nu}^2(\vec{e}_1\Lambda\vec{e}_2)\cdot\vec{R}_{12}G_{12}[\mathrm{Im}_1(\tilde{\nu})\mathrm{Re}_2(\tilde{\nu}) + \mathrm{Im}_2(\tilde{\nu})\mathrm{Re}_1(\tilde{\nu})]$$

where $\vec{e}_1$ and $\vec{e}_2$ are the unit vectors defining the polarization directions of oscillators 1 and 2, $\vec{R}_{12}$ is the distance vector between them, G_{12} is the point dipole/point dipole interaction energy, $\mathrm{Im}_i(\tilde{\nu})$ and $\mathrm{Re}_i(\tilde{\nu})$ are the imaginary and real part of the complex polarizability associated with the *i*th oscillator. In the absorption region of the chromophore (oscillator 1), where the second oscillator does not show a significant absorption (this condition is certainly fulfilled here, considering the different absorption regions of the chromophore, ~240 nm, and of the alkyl groups, ($\lambda < 150$ nm), the formula simply becomes

$$\Delta\epsilon = (48/3296)\pi^2 N\tilde{\nu}^2(\vec{e}_1\Lambda\vec{e}_2)\cdot\vec{R}_{12}G_{12}\mathrm{Im}_1(\tilde{\nu})\mathrm{Re}_2(\tilde{\nu})$$

The sign of the cd is then determined by the geometrical factor $(\vec{e}_1 x\vec{e}_2)\vec{R}_{12}G_{12}$, which is negative for C3–C4 and positive for C6–C7; in fact, they define a negative and a positive chirality,[14] respectively.

(c) Completely similar considerations can also be reported for C–H bonds; as it can be observed from Table

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[10] Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1980**, *73*, 3617.

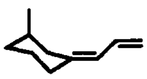
[11] Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3252.

[12] Snyder, P. A.; Johnson, W. C., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2939 and references therein.

[13] Raymonda, J. W.; Simpson, W. T. *J. Chem. Phys.* **1967**, *47*, 430.

[14] Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy*; Oxford University Press: Oxford, 1983.

Table II. Comparison between CD Experimental Data and Theoretical Results (Longest Wavelength Band)[a]

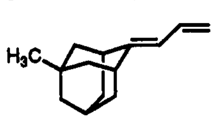
dienes	A	B	C	D	E
	+3.73	95	+	−0.36	−0.05
		5	−	+0.50	+0.07
	+5.12	100	+	−1.29	−0.10
	−5.39	87	−	+0.63	+0.32
		13	+	−2.12	−0.16
	+4.30	68	+	−0.23	−0.18
		32	−	+1.69	+0.57

[a] Key: A, experimental values, $\Delta\epsilon_{\max}$. Data taken from ref 2; B, percent of conformer in solution at room temperature (from ref 2); C, sign of the longest wavelength cd band following Walborsky's "planar diene rule"; D, results obtained with De Voe's coupled oscillators method, $\Delta\epsilon_{\max}$; E, results obtained with the CNDO/S method, $\Delta\epsilon_{\max}$.

I, only the axial allylic bonds give significant contributions, showing opposite sign because, in this case as well, opposite chiralities are formed by the two pairs of chromophore–perturbers.

(d) The overall cd, obtained taking into account all the perturbers, is −0.36 (to be compared with the value of −0.56 obtained by summing up every pairwise contribution, the difference between the two values can be attributed to many-body interactions), and it is *opposite* to the experimental value for the same absolute configuration. We also studied several allied compounds, with every one taken from the original paper of Walborsky.[2] As can be seen from Table II, for each molecule the optical activity predicted by means of De Voe calculations is always *opposite* in sign to what was experimentally found by Walborsky and co-workers.

A simple system useful to verify the internal validity of the calculations is provided by the diene 2:



2, (αR)-(+)-(5-methyladamantylidene)propene

As pointed out by Walborsky, the chirality of 2 is only due to the difference CH_3 vs H (the extraannular methyl group), so from the point of view of our calculations, this molecule can be simply treated as a diene chromophore chirally perturbed by a single C–C bond. Even in this instance, a value of −0.31 is found vs the experimental value of +0.45.

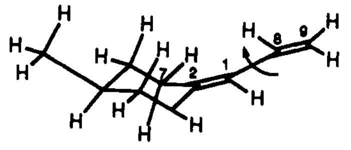
Discussion

The results of the previous calculations carried out on several s-trans dienes show that the present dynamic coupling treatment does not provide the correct sign of the cd allied to the low-energy, electrically allowed π–π^* transition in cyclohexylidenepropene derivatives. The reason of this result could be found, at least in principle, in an intrinsic failure of the model or in an unsuitable parametrization of the subsystems employed in the De Voe calculations.

The polarizability model presently adopted in all the cases previously studied always gave the correct answer in terms of sign and order of magnitude of cd bands for many different molecules such as an alkylbenzene, diacetylenes, and allenes.[9]

The spectroscopic parameters employed to describe the various subsystems might constitute a possible weak point of the present treatment. In fact, it can be observed from Table I that the allylic axial C–H bonds provide intense cd contributions, with the C_3–H_{ax} showing the strongest intensity and the right sign. The contribution of this perturber could overcome the effects due to the other bonds, leading to the overall correct sign; that could be possible, however, only if the polarizability attributed to C–H bonds is larger than the polarizability of C–C bonds. The relative importance of chirally disposed allylic hydrogen atoms or methyl groups in determining π–π^* CE in diene chromophores has been debated for a long time; different opinions can be found in the literature,[15] but most authors[12] agree that C–C polarizability is stronger than the C–H one. However, it is noteworthy that even for compound 2 the dynamic coupling cd calculated by the De Voe model (−0.31) is opposed to what is experimentally found (+0.45). It is easy to realize that in this molecule the contributions of the allylic C–C bonds are cancelling out each other by symmetry, so that the chiral perturbation giving rise to CE of the diene chromophore can only be recognized in the extrannular CH_3 group.

One might argue that other mechanisms except for the coupled oscillators one could be active in giving rise to the optical activity of these diene systems. For this reason, we decided to test a different theoretical approach, i.e., molecular orbital calculations in the CNDO/S approximation. This method has been widely used in the prediction of optical activity of relatively small organic molecules, and in several cases it has been applied to dienes.[16,17] Both Charney[16] and Bouman[17] suggest that the best agreement with the experimental data is met without using configuration interaction. The interesting feature is that the results from CNDO/S calculations always parallel the ones from De Voe's (see Table II); that is, they provide, in all the cases examined, rotatory strengths that are opposite in sign and 1 order of magnitude lower in intensity with respect to the experimental values. The experimental results can be reproduced, in the CNDO/S frame, only introducing a little torsion around the central single bond, i.e., giving rise to a dissymetric chromophore. Actually, a rotation of about 5° in the sense shown (clockwise looking from C8 to C1) provides the correct sign and order of magnitude of intensity.



But on the other hand, an equivalent rotation in the other direction leads to an equal and opposite rotational strength.

At this point, we carefully reinvestigated all the conformational features of 1: it can be seen, using a simple molecular model, that the hydrogen atom on the diene carbon 8 and the equatorial one on the annular carbon 7

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[15] Moriarty, R. M.; Paaren, H. E.; Weiss, U.; Whalley, W. B. *J. Am. Chem. Soc.* 1979, *101*, 6804.

[16] Rosenfield, J. S.; Charney, E. *J. Am. Chem. Soc.* 1977, *99*, 3209.

[17] Boumann, T. D.; Lightner, D. A. *J. Am. Chem. Soc.* 1976, *98*, 3145.

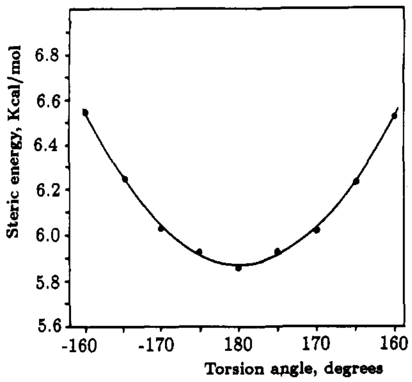

Figure 1. Energy of the diene torsion as calculated with MMP2. The rule here adopted for the diene dihedral angle is the following: looking from the carbon atom 8 to the carbon atom 1, a planar trans situation corresponds to 180° for the (9–8–1–2) dihedral angle. A clockwise rotation leads to positive values (170, 160), and an anticlockwise one leads to negative values (−170, −160).

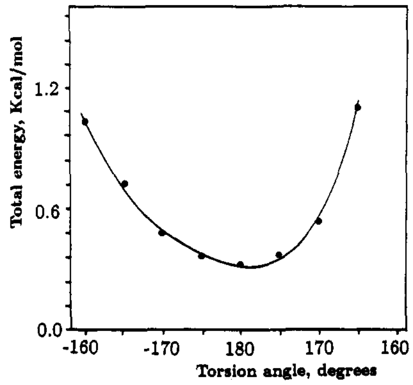

Figure 2. Energy of the diene torsion as calculated ab initio. Relative values of the energy are displayed; the zero corresponds to −40 185.8 kcal/mol. The definition of the dihedral angle is the same as in Figure 1.

come closer than the sum of their van der Waals radii. This steric strain could be overcome by a small rotation in the direction shown, leading in this way to the correct optical activity.

In order to clarify this, we used two different conformational calculation techniques: Allinger's MMP2 molecular mechanics and SCF ab initio calculations. The basis set used in ab initio calculations was the following: an optimized minimal basis set[18] for the extrannular methyl and a DZ quality one for the rest of the molecule. We used pseudopotentials for the inner shell (1s) of carbon atoms. Both the methods showed (Figures 1 and 2) that the minimum-energy conformer is the one having the diene moiety rigorously planar. This means that the decrease of the van der Waals energy between the two hydrogens is not enough to overwhelm the loss of overlap energy of the conjugate diene system, at least within the internal precision of these calculation methods.

Concluding Remarks

The most important result of our analysis is that, adapting a planar conformation of the diene moiety, we find, for every compound studied, the opposite cd sign with respect to the experimental one both with the De Voe model and with the CNDO/S one.

Taking into account that the De Voe model has been applied[7] with success to several organic molecules using the same spectroscopic description adopted here, we can conclude that the origin of optical activity in these systems cannot be found in the coupling of electric dipoles represented by the diene chromophore and the alkyl perturbers.

In a very recent paper by Walborsky and co-workers,[6] dynamic coupling calculations employing the Weigang model have been carried out. They always provide the wrong sign of the cd of chiral cyclohexylidenepropenes. As a matter of fact, it has also been reported[18] that in several new derivatives containing the planar cis diene chromophore, the Kuhn–Kirkwood dipole-coupling mechanism (i.e., the same physical considerations on which the De Voe model, here adopted, is based), cannot explain the observed cd spectra.

Assuming that the configurational assignments reported in literature are correct, what we find is that the cd calculation methods used by us can reproduce the experimental data only admitting that a twist, even slight, exists in the chromophore. In this case, a deeper conformational investigation is needed; otherwise, we have to conclude that, in spite of the large number of investigations about the origin of optical activity in the diene system, the mechanisms lying at the base of the Cotton effects in this "simple" chromophore are not yet fully understood.

Acknowledgment. We thank Prof. T. D. Bouman (Southern Illinois University, Edwardsville, IL) for kindly providing us with a copy of the CNDO/S program, interfaced with a rotatory strength calculation program.

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