Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 55–62

TETRAHEDRON:
ASYMMETRY

Circular dichroism spectra (350–185 nm) of a new series of 4-substituted [2.2]paracyclophanes: A quantitative analysis within the DeVoe polarizability model [†]

Carlo Rosini*,[a,*] Renzo Ruzziconi*,[a] Stefano Superchi,[a] Francesco Fringuelli[b] and Oriana Piermatti[b]

[a]*Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, I-85100 Potenza, Italy*
[b]*Dipartimento di Chimica, Università di Perugia, via Elce di Sotto 8, I-06100 Perugia, Italy*

Received 1 December 1997; accepted 16 December 1997

Abstract

The CD spectra of a new series of 4-substituted [2.2]paracyclophanes **1b–e** have been measured down to 185 nm. Polarizability calculations within the DeVoe model satisfactorily reproduce the CD features over all the spectral range. In addition, the analysis of the complete CD spectrum allowed a phenomenological interpretation of the dependence of the sign of $[\alpha]_D$ on the nature of the substituents, at least for X=F, OH, I. © 1998 Elsevier Science Ltd. All rights reserved.

The correlation between the chiroptical properties and structure of 4-substituted [2.2]paracyclophanes has been the subject of several investigations.[1–6] To this end, a 4-substituted [2.2]paracyclophane has been treated by Weigang and Nugent as the aggregate of two substituted benzene chromophores disposed on two different parallel planes separated by a distance *d* (Fig. 1).[2] The transitions of the two chromophores are electrostatically coupled giving rise to 'couplet' effects, and the exciton model can be employed to analyse the CD spectrum.[7] In particular, they showed that the sign of the CD in the 320–280 nm region is dependent both on the absolute configuration and on the nature of the substituent in the 4-position. However, this analysis was not extended to the other more intense transitions present in the spectra at shorter wavelengths.

A new series of 4-substituted [2.2]paracyclophanes has recently been prepared in enantiomerically pure form and it has been shown that, for the same configuration, $[\alpha]_D$ can even change sign depending on the substituent.[8] The availability of these new compounds has thus prompted us to record a complete CD spectrum (*viz.* 185–400 nm) with the aim of extending the application of the model of Weigang

---

* Corresponding author. E-mail: rosini@unibas.it

† This paper is respectfully dedicated to Prof. S. F. Mason, FRS, on the occasion of his 75th birthday, in consideration of his fundamental contribution to the development of CD spectroscopy.

0957-4166/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0957-4166(97)00522-3

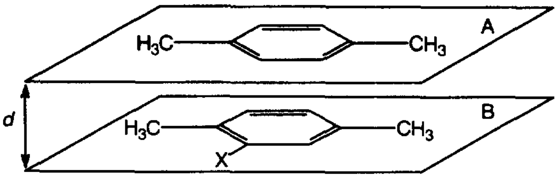


Fig. 1.

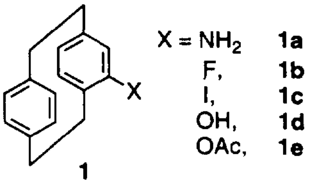


Fig. 2.

and Nugent to the above complete spectral range and of finding a correlation between CD spectra and $[\alpha]_D$, thereby providing a spectroscopic justification for the dependence of $[\alpha]_D$ on the nature of the substituent.

1. Results and discussion

(*R*)-(−)-4-Amino[2.2]paracyclophane **1a**, isolated from the racemic modification[8,9] by fractional crystallization of the diastereomeric salts of (1*S*)-(+)-camphorsulfonic acid in ethyl acetate, was used as the starting material for the synthesis of the new compounds **1b–e** (Fig. 2).[8] The stable diazonium fluoroborate **1** ($X=N_2^+BF_4^-$), prepared from **1a** by reaction with $NaNO_2$ in 40% aqueous fluoroboric acid, was transformed into **1b** by gently heating in toluene, whilst **1c** was prepared by the classic Sandmeyer reaction via the diazonium iodide **1** ($X=N_2^+I^-$).[8] The treatment of the above diazonium fluoroborate with a 1:1 mixture of acetic acid:acetic anhydride gave the corresponding acetoxy derivative **1e** from which **1d** was obtained by alkaline hydrolysis.

The most important absorption and CD features of **1b–e** are collected in Table 1. Figure 3 shows the absorption and CD spectra of **1b**, taken as a representative example. A glance at Table 1 and Fig. 3, both in the absorption and CD spectra, shows that three different absorption ranges can easily be singled out: (a) 320–270 nm; (b) 270–210 nm; and (c) 210–185 nm, which, following the analysis of Weigang and Nugent, can be related to the ^1L_b, ^1L_a and $^1B_{a,b}$ transitions of the substituted benzene chromophore.

1.1. The ^1L_b transition range

The absorption and CD data have been thoroughly analyzed by Weigang and Nugent[2] who elaborated a simple correlation between CD spectra in this range and absolute configuration of ring substituted [2.2]paracyclophanes.

Interestingly, they found that, for the same absolute molecular configuration, a positive or negative couplet can be present in the 320–270 nm range depending on the nature of X. This is a consequence of the fact that the polarization direction of the ^1L_b transition (perpendicular to the C1–C4 axis in 1,4-disubstituted benzenes) changes depending on X. With the spectroscopic moment theory of Platt[10] it is possible to predict such direction: substituents like –OH and –NH2, rotate this moment towards –X itself

Table 1
Main features of the electronic absorption and CD spectra of 4-X-substituted [2.2]paracyclophanes **1b–e**, in acetonitrile

	Absorption, ε (λ)			CD, Δε (λ)		
	^1L_b	^1L_a	$^1B_{a,b}$	^1L_b	^1L_a	$^1B_{a,b}$
1b	390 (304) 460 (286)	13,900 (225)	44,200 (188)	+4.8 (307) -2.7 (282)	-8.0 (244) +19.7 (221)	-19.4 (201) -30.0 (185)
1c	- -	14,700 (215) 9,500 (230)	29,900(197)	- -6.6 (255)	-26.3 (261) +44.1 (230)	-19.6 (206) +40.0 (188)
1d	600 (312) 450 (291)	10,200 (226)	34,000(193)	+7.3 (311) -4.5 (288)	-16.7 (250) +38.8 (228)	-29.5 (206) +32.0 (192)
1e	242 (305) 16 (286)	13,700 (224)	41,100 (191)	+1.2 (310) -1.3 (286)	-11.0 (257) +35.0 (225)	-19.7 (198) +9.5 (185)

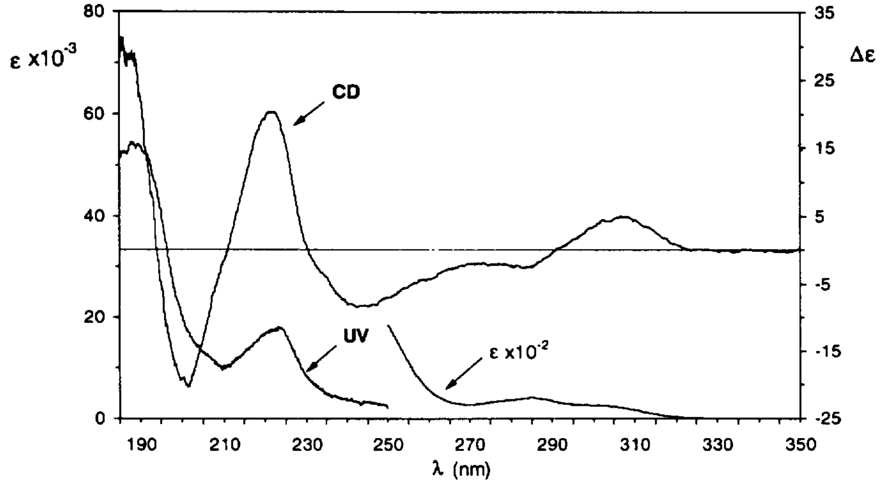


Fig. 3. The UV absorption and CD spectra of **1b** in the 350–185 nm range

(they possess a positive spectroscopic moment, in the Platt language[11]), whilst groups like –COOH and –CF_3 rotate this moment in the opposite direction (Fig. 4). Therefore, for the same absolute configuration (say *R*, Fig. 4) the dipole on the unsubstituted benzene rings has a different orientation with respect to that of the substituted ring and then different CD results. The Harada–Nakanishi chirality rules[7b,d] provide the sign of the CD couplets: for *R* configuration, substituents with positive spectroscopic moments give rise to a positive CD couplet, whilst those having negative spectroscopic moments exhibit a negative CD couplet. As can be seen from Table 1 and Fig. 3, (*R*)-**1b**, (*R*)-**1d**, and (*R*)-**1e** show a clear positive couplet in the region 320–270 nm (note in particular, that the exciton components are well resolved in the absorption spectrum in the case of (*R*)-**1b**); they, in fact, possess substituents having positive spectroscopic moments, thus indicating that the Weigang–Nugent rule is obeyed. Only for compound (*R*)-**1c** is the positive couplet not clearly observed.

A possible interpretation could be as follows: the couplet effect could be cancelled by the stronger negative band centered at shorter wavelength and related to the ^1L_a transition (*vide infra*). This cancellation

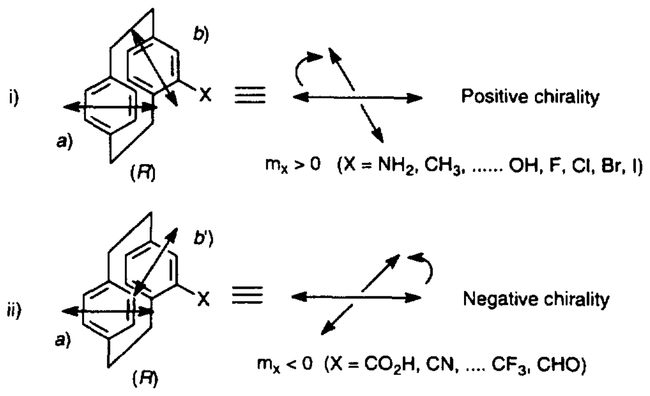


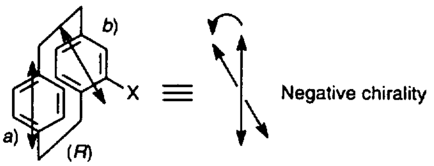
Fig. 4. Coupling of the ^1L_b transition electric dipole moments. (i) The X substituent possesses a positive spectroscopic moment ($m_X>0$) and the ^1L_b transition moment is directed as depicted. It couples with the corresponding dipole in the 1,4-dialkyl substituted chromophore leading to a positive chirality, and then to a positive CD couplet, for the *R* absolute configuration depicted. (ii) In the case of a substituent with $m_X<0$, the transition dipole moment of (*b*′) is rotated by about 90°. The dipole of (*a*) and (*b*′) now define a negative chirality and a negative couplet results for *R* absolute configuration

effect is operative only in this case probably for two reasons: (a) in (*R*)-**1c** a particularly intense Cotton effect at 265 nm is present, which overlaps quite effectively the Cotton effects in the range 320–280 nm; (b) a relatively low value ($\gg$13)[11] for the spectroscopic moment of I, lower than that of F ($\gg$21) and OH ($\gg$33), which induces low extinction coefficient in the ^1L_b transition and then a low intensity in the CD spectrum.[12]

1.2. The ^1L_a transition range

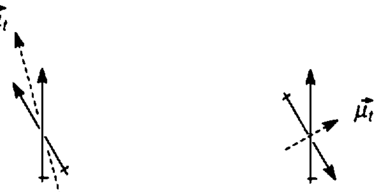
Weigang and Nugent observed in 1969 that the $^1A \rightarrow {}^1L_a$ transition gives "the same pattern of the rotatory strength signs for a given absolute configuration regardless of the substituent moment".[2] In particular, their data, those of Schlögl et al.,[3] as well as the present ones (Table 1), reveal that in the (*R*) series a negative couplet is always observed in the CD spectrum in the 200–260 nm range, i.e. corresponding to the $^1A \rightarrow {}^1L_a$ transition of the substituted benzene chromophore. This finding, which is very important for the organic chemist as it suggests a very direct relationship between the CD spectrum and the absolute configuration, was not interpreted by Weigang and Nugent and an attempt at understanding its origin will therefore be provided here, applying once again the model depicted in Fig. 1, and referring now to the coupling of the ^1L_a transitions of 1,4-dimethylbenzene and a 1-X-substituted-2,5-dimethylbenzene. Of course, this requires a knowledge of the polarization direction of this transition. It is well known that in the 1,4-dimethylbenzene moiety the ^1L_a transition is polarized along the C(1)–C(4) axis.[13,14] The second chromophore can be treated as 1-fluoro-2,5-dimethylbenzene **2b**, 1-iodo-2,5-dimethylbenzene **2c**, 1-hydroxy-2,5-dimethylbenzene **2d**, 1-acetoxy-2,5-dimethylbenzene **2e**, as far as the new compounds are concerned, whilst 2,5-dimethylbenzoic acid **2f**, and 2,5-dimethylaniline **2a**, are the chromophores of **1f** and **1a**, respectively whose CD spectra have been reported by Schlögl.[3]

The carbonyl group and the amino group strongly perturb the benzene chromophore and, as a result, a new electrically allowed π–π* transition is present at about 230 nm in the absorption spectrum of benzoic acid and aniline.[11,15] This absorption band is polarized along the axis joining the aromatic ring to the substituent. Methyl groups in the ortho positions of the benzene ring do not affect this transition; the spectra of 2,5-dimethylbenzoic acid and 2,5-dimethylaniline are, in fact, very similar[11,15] to those of the parent compounds and we can thus safely assign the same polarization direction in the chromophores **2f**



X = NH_2, CO_2H, OH, OAc, F, Cl, I

Fig. 5. Exciton chirality defined by the two ^1L_a transition dipole moments in an (*R*)-4-substituted [2.2]paracyclophane



High energy coupling mode,
High $|\mu_t|$

Low energy coupling mode,
Low $|\mu_t|$

Fig. 6. The two coupling modes of the ^1L_a transition dipole moments: the high energy coupling mode provides a higher $|\mu_t|$ than the low energy one

and **2a**. Taking into account that the perturbation is particularly strong for groups having a low ionization potential like $-NH_2$,[11] we can also immediately extend the same conclusion to the iodo-derivative **2c**. The remaining compounds **2b**, **2d**, and **2e** present groups having higher ionization potentials and they will therefore exert a smaller perturbation on the aromatic π electrons, thus, even if the transition dipole moment is not directed along the C_{Ar}–X axis (for X=F, OH, OAc), it will be turned toward X, with respect to the direction C(1)–C(4) in the unsubstituted chromophore. As shown in Fig. 5, the transition dipole moment of the ^1L_a transitions in the two chromophores define a negative chirality if the absolute configuration of the paracyclophane skeleton is *R* and a negative couplet is then to be expected in this spectral region, as found experimentally. Since the polarization direction does not depend on the particular nature of the substituent (i.e. on its spectroscopic moment), in contrast to what happens in the ^1L_b spectral range, as we saw before, a negative couplet around 230 nm is allied to the *R* configuration in 4-substituted [2.2]paracyclophanes.

It may be noted that the electronic spectra of compounds **1b–e** are characterized by an absorption maximum at about 225–230 nm, followed by a long tail extending up to 260 nm, whilst in the CD spectrum two bands of opposite sign, but very similar intensity, can be observed. In other words, it seems that the low energy component of the couplet shows a significantly lower UV intensity than the high energy counterpart. This observation is still a consequence of the exciton coupling of the ^1L_a transitions: looking at Fig. 6 it can be seen that the two transition dipole moments define a small dihedral angle. The high and low energy coupling modes are therefore characterized, simply for geometrical reasons, by large and small transition dipole moments, respectively.[16]

In order to confirm these simple qualitative considerations, some coupled oscillator calculations using the DeVoe model,[17] have been carried out taking the case of **1b** as illustrative. To this end the paracyclophane structure was schematized by two substituted benzene rings: 1,4-dimethylbenzene, (A) and 1-fluoro-2,5-dimethylbenzene (B), disposed on two planes parallel to each other (Fig. 1). The ^1L_a transition of the A ring was described employing a single oscillator centered in the benzene ring and directed along the C(1)–C(4) axis and carrying $8D^2$ at 225 nm, whilst the same transition in the B ring was directed along the axis C_{Ar}–F and carrying the same polarizability as the A ring. As a result, a negative CD couplet was obtained having $\Delta\varepsilon$ −35 at 231 nm and +35 at 219 nm. Furthermore, the calculated absorption spectrum of the 'dimer' A/B shows a maximum (ε_{max} 13,300) exactly in correspondence with the high energy part of the couplet, whilst the absorption intensity is only 7900 in correspondence with the low energy part of the couplet. These results are in satisfactory agreement with the experimental data (Table 1, Fig. 3), thus supporting the validity of the simple representation of the paracyclophane structure given in Fig. 1 and, at the same time, also suggesting the correctness of the assignment of the polarization direction of the ^1L_a band for the substituted benzene chromophores made here.

1.3. *The $^1B_{a,b}$ transition range*

The absorption and CD spectra of derivatives **1b**–**e** are also very similar in this range. These compounds, in fact, exhibit a very intense band in absorption centered at about 190–195 nm ($\varepsilon_{max} \approx 40,000$), whilst a negative couplet (having extremes in the range −20 to +30) is observed between 200 and 185 nm. It is well accepted[13,14] that the 200–185 nm spectral range in benzene is dominated by the $^1A_{1g} \rightarrow {}^1E_u$ transition (using the symmetry labels of benzene, D_{6h} point group) which gives rise to two orthogonal, degenerate transition moments. A systematic investigation by Sagiv[14] has shown that, in general, these two transition dipoles remain degenerate and orthogonal even in the presence of strongly perturbing substituents (such as OCH_3, for instance). One could, therefore, think that the spectral features observed in this region are due to the coupling of the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition dipole moments, according to the model used up to now to analyze the ^1L_b and ^1L_a spectral region. Attempts at reproducing the CD features in this region were then carried out by means of DeVoe calculations, again employing the simplified model depicted in Fig. 1. However, if the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition of each benzene ring is represented by two equal dipoles located in the center of each ring and directed along the axis joining the positions involved in the paracyclophane linkage (i.e. the axis joining atom 3 and atoms 6) for the former and orthogonal to it in the same plane for the latter, we have a structure which shows a symmetry plane and then cannot show optical activity. Rotation of a dipole pair (that of B in Fig. 1, for instance) by an angle θ with respect to the pair in A does not describe a dissymmetric structure because, as long as the two dipoles of a pair remain orthogonal and degenerate, they describe the same situation.[18] As a matter of fact, DeVoe calculations always provided zero CD. The further inclusion in the calculation of the dipoles related to the ^1L_a transitions in each ring led to a very important result: a negative couplet appeared (i.e. like the one found experimentally) even if the calculated CD intensity (−2; +2) is about an order of magnitude smaller than the experimental one. Some other attempts were then made at improving the calculated intensity of the $^1B_{a,b}$ transition. The investigations of Sagiv showed that the 180–200 nm band of benzene derivatives is made by two orthogonal, degenerate components which remain such even in the presence of strongly perturbing substituents. Actually this degeneracy could be removed by a distortion from planarity, like that present in the paracyclophanes. In fact, a standard CNDO/S–CI calculation on a fluorobenzene in which this distortion has been introduced showed that the two allowed components of the 180–200 nm transition are no longer degenerate, but separated by about 2,000 cm^{-1}. Then the above described calculation was repeated introducing a separation of 2,000 cm^{-1} in the energy position of the two polarizabilities thus obtaining a significant improvement, as the intensities of the $^1B_{a,b}$ couplet became (−6; 5).

The results obtained in this investigation have shown that the exciton coupling between the A and B moieties (Fig. 1), as originally proposed by Weigang and Nugent, constitutes the main mechanism by which the optical activity of these compounds can be accounted for, throughout the whole 185–350 nm spectral range. In particular, it was shown that the CD intensity in the ^1L_a range can be satisfactorily reproduced by the DeVoe calculations and that the absolute configuration is immediately related to the sign of the CD couplet in this range, independent of the nature of the substituent in the 4 position. As far as the $^1B_{a,b}$ spectral range is concerned, we could reproduce correctly the sign of the couplet but only a fraction of the experimental intensity.

In conclusion, we may try to provide some interpretation of the change in sign of $[\alpha]_D$ depending on the nature of the substituent; the comparison between **1b** and **1c** looks particularly suitable. The data reported in Table 1 and Fig. 3 suggest that the sign of $[\alpha]_D$ depends on a delicate balance of the contributions (at 589 nm) due to the ^1L_b and ^1L_a Cotton effects. A substituent like –F, provided with a high positive spectroscopic moment, induces a significantly intense positive couplet in the ^1L_b region (the result then being a positive contribution at 589 nm). This effect is not overwhelmed by the negative contribution due to the negative branch of the ^1L_a couplet, which is located quite a long way away (244 nm) on the wavelength scale. The situation is very different in the case of **1c**: here, the ^1L_b Cotton effect is completely overwhelmed by the strongly negative ^1L_a Cotton effect, which, in addition, is now located at 261 nm and thus nearer (when compared with the similar effect in **1b**) to the sodium D line. In other words, in general an (*R*)-paracyclophane will show a negative rotation power at 589 nm: a positive $[\alpha]_D$ can only result if the strong contribution at 589 nm due to the negative couplet allied to ^1L_a transition is overwhelmed by a positive contribution due to the ^1L_b transition. This fact can occur for substituents X, like –F and –OH,[19] which possess a strong positive spectroscopic moment, and therefore induce a significant positive couplet in the ^1L_b region.

2. Experimental section

Compounds **1b–e** were obtained by the procedure described by Cipiciani et al.,[8] the enantiomeric purity of the samples ranged between 85 and 95%. Absorption and CD spectra were recorded on a JASCO J600 spectropolarimeter at room temperature, in acetonitrile, using 0.1 and 10 mm cell and concentrations in the order of 1×10^{-3} M. During the measurement, the instrument was thoroughly purged with nitrogen.

Acknowledgements

The authors thank Prof. M. Zandomeneghi of the Dipartimento di Chimica e Chimica Industriale, Università di Pisa, for his constructive criticism in reading the manuscript. Thanks are also due to Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR) for financial support.

References

1. Falk, H.; Schlögl, K. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 383.
2. Weigang, O. E.; Nugent, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 4555, 4557.
3. Falk, H.; Reich-Rohrwig, P.; Schlögl, K. *Tetrahedron* **1970**, *26*, 511.
4. Tochtermann, W.; Vagt, U.; Snatzke, G., *Chem. Ber.* **1985**, *118*, 1996.
5. Several relevant papers recently appeared by F. Vögtle et al. where the CD spectra of other paracyclophanes have been described. See, for instance, Pischel, I.; Nieger, M.; Archut, A.; Vögtle, F. *Tetrahedron* **1996**, *52*, 10043.
6. Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1955**, *77*, 6289.
7. (a) Mason, S. F. "Molecular Optical Activity and the Chiral Discriminations", Cambridge University Press, Cambridge, 1982; (b) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry", University Science Books, Mill Valley, CA, 1983; (c) Nakanishi, K.; Berova, N. in "Circular Dichroism: Principles and Applications" Nakanishi, K.; Berova, N.; Woody, R. W., Eds., VCH Publishers, New York, 1994, chap. 13, p. 361; (d) A

different approach, alternative to the chirality rules has been recently introduced. See: Rodger, A.; Norden, B. "Circular Dichroism and Linear Dichroism" Oxford University Press, Oxford, 1997.

8. Cipiciani, A.; Fringuelli, F.; Mancini, V.; Piermatti, O.; Pizzo, F.; Ruzziconi, R. *J. Org. Chem.* **1997**, *62*, 3744.
9. Beak, P.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc.* **1986**, *108*, 6016.
10. Platt, R. J. *J. Chem. Phys.* **1951**, *19*, 263; Petruska, J. *J. Chem. Phys.* **1961**, *34*, 1111, 1120. The sign (positive or negative) of the spectroscopic moment in a di- or tri-substituted benzene chromophore determines the orientation, within the chromophore itself, of the transition dipole moment of the ^1L_b.
11. Murrel suggests a value of spectroscopic moment for I (+13) significantly lower than the original one (+21) of Platt (see Ref. 10). Murrel, J. N. "The Theory of Electronic Spectra of Organic Molecules" Methuen, London, 1963, p. 207.
12. The amplitude of a CD couplet is proportional to $\varepsilon_{\max}$ of the chromophore involved (See Ref. 7b and Heyn, M. P. *J. Phys. Chem.* **1975**, *79*, 2424).
13. Michl, J.; Thulstrup, E. W. "Spectroscopy with Polarized Light", VCH Publishers Inc., New York, 1986.
14. Sagiv, J. *Tetrahedron* **1977**, *33*, 2303.
15. Suzuki, H. "Electronic Absorption Spectra and Geometry of Organic Molecules" Academic Press, Oxford, 1967: pp. 476 and 485.
16. Rosini, C.; Rosati, I.; Spada, G. P. *Chirality* **1995**, *7*, 353.
17. In the DeVoe model a molecule is considered to be composed of a set of subsystems, the chromophores; they are polarized by the external electromagnetic radiation and are coupled to 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 interaction of the subsystems. Therefore, this treatment requires a division of the molecule into a set of subsystems that have to be suitably characterized. Then, each group is represented in terms of one or more classical oscillator(s); each oscillator represents an electric-dipole-allowed transition, defined by the polarization direction $\mathbf{e}_i$ and the complex polarizability $\alpha_i(\nu)=R_i(\nu)+I_i(\nu)$. $I_i(\nu)$ is obtainable from the experiment, from the absorption spectra of the compounds that can be considered good models of the subsystem, and $R_i(\nu)$ can be calculated from $I_i(\nu)$ by means of a Kronig–Kramers transformation. From the general formulation of the DeVoe model, retaining only the terms to first order in G_{12} (physically, this means considering that the electric dipole on the i chromophore is caused by the external e.m. field plus the dipolar fields of the other dipole polarized by the external field only) the following expression can be deduced in the case of two different chromophores having only one electrically allowed transition each which provides CD as a frequency function is: $\Delta\varepsilon(\nu)=0.014\pi^2 N\mathbf{e}_1 X\mathbf{e}_2 R_{12} G_{12}\ \nu^2[I_1(\nu)R_2(\nu)+I_2(\nu)R_1(\nu)]$; $G_{12}=(1/r_{12})^3[\mathbf{e}_1.\mathbf{e}_2 - 3(\mathbf{e}_1\mathbf{e}_{12})(\mathbf{e}_2\mathbf{e}_{12})]$. Here $\mathbf{e}_1$, $\mathbf{e}_2$ are the unit direction vectors of the transition dipole moments of the first and second chromophore, respectively, R_{12} is the distance between them, G_{12} is the point-dipole–point-dipole interaction term. This expression gives rise to a couplet-like feature if the absorption maxima of the chromophore 1 and 2 are near in frequency ("quasidegenerate" coupled oscillator system). DeVoe, H. *J. Chem. Phys.* **1964**, *41*, 393; *ibidem* **1965**, *43*, 3199. For some applications of these calculations to structural problems see: Rosini, C.; Salvadori, P.; Zandomeneghi, M. *Tetrahedron: Asymmetry* **1993**, *4*, 545
18. Shingu, K.; Imajo, S.; Kuritani, H.; Hagishita, S.; Kuriyama, K. *J. Am. Chem. Soc.* **1983**, *105*, 6966.
19. (*R*)-4-Amino[2.2]paracyclophane is levorotatory at 589 nm (see Ref. 8) even if the amino group possess one of the largest values (+3) of the spectroscopic moment. This happens because the NH_2 group exerts a strong perturbation in the ^1L_a range as well giving rise to very intense negative ^1L_a couplet.