

Concerning the Applicability of a Chirality Function to Different Chirality Observables**

Elisabeth Langer and Harald Lehner*

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

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The applicability of a chirality function for the description of a special chiroptical property of a class of compounds does not imply its sufficiency for other observables of optical activity. Notwithstanding the fact, that molar rotations ($[M]_{\lambda}$) can be understood in terms of contributions from electronic transitions, a chirality function consistent with the optical rotations of a kind of molecules may turn out inadequate for the circular dichroism (cd). This is demonstrated by means of $[M]$ and cd data of optically active 5,5'-disubstituted 2,2'-spirobiindanes.

(Keywords: Circular dichroism; Chirality function; 2,2'-Spirobiindanes)

Zur Anwendbarkeit einer Chiralitätsfunktion für verschiedene Chiralitätsbeobachtungen

Die Anwendbarkeit einer Chiralitätsfunktion zur Beschreibung einer bestimmten chiroptischen Eigenschaft einer Molekülklasse impliziert keineswegs auch deren Gültigkeit für andere Chiralitätsbeobachtungen. Ungeachtet der Tatsache, daß Molrotationen ($[M]_{\lambda}$) aus Einzelbeiträgen elektronischer Übergänge zusammengesetzt sind, kann es vorkommen, daß eine Chiralitätsfunktion, die den optischen Drehwerten einer Molekülklasse genügt, für den Circular dichroismus (CD) ungeeignet ist. Dies läßt sich anhand von $[M]$ und CD-Daten optisch aktiver 5,5'-disubstituierter 2,2'-Spirobiindane zeigen.

Introduction

The algebraic theory of chirality functions^{1,2} represents an exceptional approach to the chirality phenomenon. The concept deals with the permutational and symmetry behaviour of suitably chosen molecular skeletons and pertinent assortments of ligands. Physical

* Dedicated to Professor *O. E. Polansky* on the occasion of the 60th anniversary of his birthday.

** Concerning the Theory of Chirality Functions, part 6; for parts 4 and 5 cf. ref.³.

properties of the molecules (such as the nature of the chromophore or the transitions involved) are not included and cannot furnish criteria for its range of validity. Therefore the principal applicability of the algebraic theory is almost unlimited. The chirality functions deduced via the approximation procedures ("Näherungsansätze") proposed in ^{1,2} are the mathematically most simple ones out of an unlimited number fulfilling the necessary symmetry requirements³. On their application the physical character of a chiroptical property can only be taken into consideration *a posteriori* by means of distinct values of ligand parameters, which may be determined experimentally.

With respect to these approximations a suitable restriction concerning the number of ligand-sorts results in most cases in an annihilation of higher terms. Consequently, for a special observable each kind of ligand is qualified by a single parameter.

Since the concept refers to any chiroptical property the adoption of a single chirality function—*e. g.* a polynomial deduced by the method given in²—for the description of all optical activity observables within a given skeleton class is justified. On the other hand the consistency of all these data with the same function would imply their different qualities manifesting themselves merely in varying sets of ligand parameters. Clearly, while the theory does not forbid a general application of a single chirality function, it does by no means predict the success of such an approach. Bearing in mind the abundance of chiroptical phenomena, this sufficiency of a single approximation function is of low probability. To derive however a physical interpretation of a given chirality function it will in most cases be favourable to expound its range of validity. Up to date practical applications of chirality functions have almost exclusively been devoted to molar rotations⁴⁻⁹. A comparison of different chirality observables was performed by means of molar rotations⁸ and cd data of substituted [2.2]metacyclophanes¹⁰.

The molar rotations of 5,5'-disubstituted 2,2'-spirobiindanes were shown to be in excellent agreement with the pertinent polynomial⁶. The cd data of these compounds have recently been published¹¹. Taking into account the coherence of optical rotation with components of electronic transitions¹² a similarly good agreement of the chirality function with the cd *Cotton* effects of 2,2'-spirobiindanes might be expected. This will be examined in our study.

Results and Discussion

The cd data of **1 a-j** are given in¹¹. Remeasurement in an apolar solvent (isooctane) showed negligible solvent effects. Tab. 1 contains the $\Delta \epsilon_{\max}$ values¹¹, rotational strengths and contributions to the molar

Table 1. Chirality observations $\Delta\epsilon_{\max}^a$, R_i^b and M_i^b derived from the cd of **1a-j** and molar rotations $[M]_D^c$

	λ_{\max}	$\Delta\epsilon_{\max}$	1L_a $R \times 10^{40}$ d	$M_{L_a,D}$	λ_{\max}	$\Delta\epsilon_{\max}$	1L_b $R \times 10^{40}$ d	$M_{L_b,D}$	$[M]_D$
1a	228	+ 1.41	+ 1.9	+ 30	279	- 0.11	- 0.11	- 2.9	+ 11.4
1b	228	+ 1.45	+ 1.9	+ 30	277	- 0.10	- 0.12	- 3.1	+ 19.3
1c	264	+ 10.79	+ 13.2	+ 303	290	+ 2.00	+ 3.81	+ 111.2	+ 90.6
	247	- 11.83	- 16.5	- 322					
1d	252	+ 9.70	+ 11.4	~ 0	288	+ 1.02	+ 1.46	+ 42.0	+ 73.0
	235	- 9.61	- 12.3						
1e	251	+ 12.07	+ 12.4	~ 0	288	+ 1.36	+ 1.91	+ 55.0	+ 84.7
	235	- 10.52	- 12.2						
1f	257	+ 9.43	+ 13.5	+ 290	287	+ 1.80	+ 2.16	+ 61.5	+ 88.3
	240	- 10.96	- 14.7	- 268					
1g	227	+ 1.06	+ 1.6	+ 26	279	- 0.08	- 0.09	- 2.4	+ 15.7
1h	254	+ 1.72	+ 4.4	+ 91	284	+ 0.22	+ 0.40	+ 11.1	+ 42.9
1i	236	+ 2.22	+ 5.6	+ 103	282	+ 0.15	+ 0.25	+ 6.7	+ 39.1
1j	238	+ 2.14	+ 4.6	+ 84	288	+ 0.17	+ 0.24	+ 6.9	+ 41.3

^a The values are taken from¹¹ and refer to ethanolic solutions. The parameters derived from the cd of **1a-j** in isoctane are within $\pm 5\%$ (Jobin Yvon, Mark III circular dichrograph; for experimental details cf.^{10,11}). ^b For the calculation cf.¹⁰. Error $\leq 20\%$. ^c Taken from⁶. ^d [$\text{erg} \cdot \text{cm}^3$].

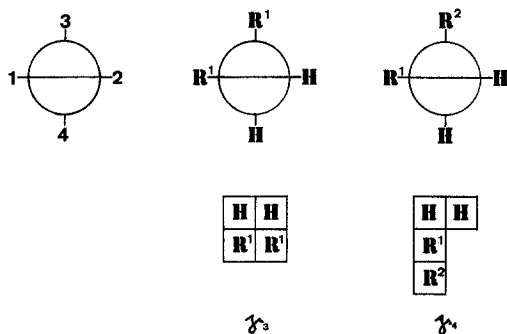


Fig. 1. Numbering, configuration and correlated assortment diagrams of the 2,2'-spirobiindanes **1 a-j**

rotations for the 1L_a and 1L_b electronic transitions. For a comparison the molar rotations $[M]_D^6$ are included as well.

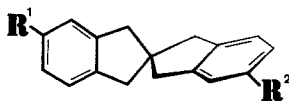
The 2,2'-spirobiindanes **1 a-j** belong to the assortment diagrams γ_3 and γ_4 (cf. Fig. 1). For these derivatives the chirality function

$$\chi = \varepsilon \cdot (l_1 - l_2) \cdot (l_3 - l_4), \quad \varepsilon = \pm 1 \quad (1)$$

has most successfully been applied to the molar rotations⁶. In accord with² we may choose $l_H = 0$. Therefore we derive from (1)

$$\chi = \varepsilon \cdot l_1 \cdot l_3 \quad (1a)$$

For a test of this function at least three compounds are required. Such



	R¹	R²
1 a	CH ₃	CH ₃
1 b	C ₂ H ₅	C ₂ H ₅
1 c	COCH ₃	COCH ₃
1 d	COOH	COOH
1 e	COOCH ₃	COOCH ₃
1 f	COOCH ₃	COCH ₃
1 g	C ₂ H ₅	CH ₃
1 h	C ₂ H ₅	COCH ₃
1 i	C ₂ H ₅	COOH
1 j	C ₂ H ₅	COOCH ₃

triples are represented by the sets $\mathbf{1a/1b/1g}$, $\mathbf{1c/1e/1f}$, $\mathbf{1b/1c/1h}$, $\mathbf{1b/1d/1i}$, and $\mathbf{1b/1e/1j}$ respectively, each containing two *homodisubstituted* derivatives and the pertinent *hetero*-compound. Thus, our discussion will initially be restricted to a separate treatment of these five triples.

Equation (1a) demands that for the two *homodisubstituted* compounds out of each set the chirality observation chosen should be equal in sign. Furthermore (1a) claims that, if an occasional zero point* occurs for one member, it should also be observed in the other two compounds. With respect to the actual discussion only single or split bands should be observed for a given electronic transition but not both.

An inspection of the chirality observations gained from the 1L_a and 1L_b Cotton effects clearly shows (cf. Tab. 1) that these conditions are only fulfilled by $\mathbf{1a/1b/1g}$ and at least qualitatively by $\mathbf{1c/1e/1f}$, while for $\mathbf{1b/1c/1h}$, $\mathbf{1b/1d/1i}$, and $\mathbf{1b/1e/1j}$ the restrictions implied by (1a) are not at all met in either of the two bands.

Extending our treatment to all derivatives listed in Tab. 1 the implications of (1a) given above for triples should remain valid, so that common zero points for *all* derivatives and a constant sign for a given observable for *all homodisubstituted* derivatives should be found. However, even on comparing only the two triples $\mathbf{1a/1b/1g}$ and $\mathbf{1c/1e/1f}$ —consistent with (1a) within themselves—these conditions are not met. Different signs of ϵ would be required for the 1L_b band of $\mathbf{1a/1b}$ and $\mathbf{1c/1e}$ respectively, while the 1L_a transition, being monosignate for $\mathbf{1a/1b/1g}$ is bisignate for $\mathbf{1c/1e/1f}$.

This latter behaviour has been explained by means of the excitation chirality model¹¹. The inhomogeneity of sign of the 1L_b bands signifies in other words, that this Cotton effect is not configuration specific. This poor correlation between the absolute configuration and the sign of cd bands owing their rotational strength to forbidden character vibronic coupling is not surprising and has been rationalized on a quantum mechanical basis¹³.

On the other hand, considering the mutual correlation of ord and cd¹² and the excellent agreement of the molar rotations of $\mathbf{1a-j}$ with the polynomial (1a) its insufficiency for their cd data is rather unexpected. Comparison of the $[M]_j$ and $[M]_D$ values (cf. Tab. 1) gives evidence, that the combined 1L_b and 1L_a electronic transitions furnish an important contribution to the molar rotations at 589 nm.

* An occasional zero point corresponds to a vanishing chirality observable, e.g. the inflection point of a couplet within a cd band.

Nevertheless an interpretation of the nonconformity of $[M]_D$ and *cd* data on the basis of the *Rosenfeld* equation¹² could only be given by including remote transitions, which are beyond the normal range of experimental techniques as yet.

On the other hand, bearing in mind the parallels in the chiroptical properties of the two bichromophoric systems a comparison with the above mentioned investigation concerning [2.2]metacyclophanes suggests itself^{10,11}. While the different arrangements of the benzene chromophores in the two systems (D_{2d} and C_{2h} respectively) are reflected in their rotational strengths, the generation of 1L_b and 1L_a optical activity can be described by the same physical model. A vibronic perturbation is responsible for the 1L_b *Cotton* effect of all derivatives. The same is true for the 1L_a transition only if at least one of the ligands does not exhibit a large spectroscopic moment. Dipole-dipole coupling is observed, if each of the two benzene moieties shows strong electronic interaction with the substituent. Due to the lower symmetry of the metacyclophane skeleton however the appropriate chirality polynomial is a simple superposition rule¹⁴. In contrast to the behaviour of **1 a-j** the intrinsic relationship of *ord* and *cd* is clearly manifest with respect to the suitability of this function^{8,10}. The few derivatives exhibiting an additive dependence of molar rotations on ligand parameters are equally consistent with the linear polynomial in the *entire* frequency range accessible, while the sufficiency of the function for a *single* transition is by no means concomitant with its applicability to $[M]_D$. Evidently the linear chirality function deduced for the C_{2h} skeleton of [2.2]metacyclophanes is much more sensitive to the additive contributions from absorption bands contained in the *Kronig Kramers* transforms than the chirality product (1).

Apart from 2,2'-spirobiindanes the polynomial (1) has most successfully been applied to the molar rotations of optically active allenes⁴. Since their electronic transitions are of different nature, an analogous analysis of their *cd* spectra given in¹⁵ would be of great interest.

One might argue* that the chirality functions according to^{1,2} are only deduced for the static skeleton symmetry, *i. e.* D_{2d} for **1 a-j** and C_{2h} for the metacyclophanes investigated in¹⁰. Hence, since the transitions considered are symmetry forbidden and thus *Cotton* effects are generated by mixing with low symmetry vibrations this concept might fail. Bearing in mind the *Rosenfeld* equation¹² the excellent agreement between (1 a) and the molar rotations of **1 a-j** in the transparency region would then only be explicable by assuming that $[M]_D$ is exclusively determined by allowed far-uv transitions. In this case, however, one

* We thank Prof. *P. Schuster* for this suggestion.

should expect that the contributions $[M]_i$ from the 1L_a and 1L_b Cotton effects are small compared to the $[M]_D$ values, in disagreement with experimental data (cf. Tab. 1). Besides, for the mono- and dimethyl-[2.2]metacyclophanes given in¹⁰ the cd in the accessible wavelength region conforms satisfactorily with the pertinent chirality function.

The foregoing study does not exclude a description of chirality observations gained directly from the cd of 2,2'-spirobiindanes. However, a chirality function consistent with the data would have to be more complex than (1). Alternatively a different approach, which has recently been proposed by Pančoska¹⁶ on the basis of a subspectral analysis might be promising.

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