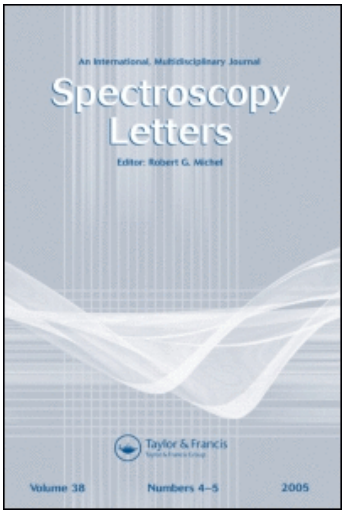
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Magnetic Circular Dichroism of Cyclic π-Electron Systems

Josef Michl[a]
[a] Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität, Münster, Germany

To cite this Article Michl, Josef(1977) 'Magnetic Circular Dichroism of Cyclic π-Electron Systems', Spectroscopy Letters, 10: 6, 509 — 517
To link to this Article: DOI: 10.1080/00387017708065508
URL: http://dx.doi.org/10.1080/00387017708065508

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 10(6), 509-517 (1977)

MAGNETIC CIRCULAR DICHROISM OF CYCLIC π-ELECTRON SYSTEMS

Josef Michl[1]

Organisch-Chemisches Institut der Westfälischen
Wilhelms-Universität, Münster, Germany

Downloaded At: 04:24 30 January 2011

ABSTRACT

While the simple PPP model accounts for the absolute signs of low-energy ππ* transitions in cyclic π-electron chromophores (numerous new examples of application to heterocycles are given), its greatest contribution lies in the formulation of simple general rules. The previously known mirror-image pairing theorem for charged alternant hydrocarbons and the soft-hard rule for substituent and heteroatom effects on cyclic π-systems are now complemented by a ΔHOMO-ΔLUMO rule which permits prediction of the absolute sign of the lowest energy B term in cyclic π-systems which are formally related to an annulene containing 4N+2 electrons.

INTRODUCTION

Magnetic circular dichroism (MCD) provides a measure of the difference between absorption of left-handed circular polarized light and right-handed circular polarized light propagating along the direction of the magnetic

Copyright © 1977 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

field. The customary measure of MCD intensity of a transition 0→F between non-degenerate states in isotropic solution, the so-called B term, is related to the area under the MCD peak (in the absence of vibronic effects its shape follows that of the absorption peak):

$$B = -33.53^{-1} \int d\tilde{\nu} [\theta]_M / \tilde{\nu} \qquad (1)$$

where $[\theta]_M$ is molar ellipticity per unit field in deg. l. m^{-1}. mol^{-1}. $gauss^{-1}$, and $\tilde{\nu}$ is the wavenumber. Note that the B term is positive if the MCD peak is negative. In the electric dipole approximation[2],

$$B(0\to F) = \sum_{I\neq 0,F} B^F_{I,0} + \sum_{I\neq 0,F} B^F_{I,F} + (B^F_{F,0} + B^F_{0,F}), \qquad (2)$$

where

$$B^F_{I,0} = \langle I|\vec{\mathcal{M}}/i|0\rangle . \langle 0|\vec{M}|F\rangle \times \langle F|\vec{M}|I\rangle / (E_I - E_0),$$

$$B^F_{I,F} = \langle F|\vec{\mathcal{M}}/i|I\rangle . \langle 0|\vec{M}|F\rangle \times \langle I|\vec{M}|0\rangle / (E_I - E_F), \qquad (3)$$

$$B^F_{F,0}+B^F_{0,F} = \langle F|\vec{\mathcal{M}}/i|0\rangle . \langle 0|\vec{M}|F\rangle \times (\langle F|\vec{M}|F\rangle - \langle 0|\vec{M}|0\rangle) / (E_F - E_0).$$

Here, the sums run over all electronic states except as indicated, $\vec{\mathcal{M}}$ is the magnetic and $\vec{M}$ the electric dipole moment operator, and E_A is the energy of A-th state. The contribution $(B^F_{F,0}+B^F_{0,F})$ is usually small, since it requires that the transition 0→F be simultaneously magnetic dipole and electric dipole allowed and further requires a change in the permanent dipole moment upon excitation. Also, the contributions $B^F_{I,0}$ are usually relatively small, since the energy denominator $E_I - E_0$ is large for ordinary molecules

Downloaded At: 04:24 30 January 2011

compared to E_I-E_F for at least some states I. Frequently then, mixing with just a few states I which are near in energy dominates the signs of B terms. General theory[2] also allows for the case of highly symmetrical molecules with degenerate ground and/or excited states, which yields the so-called A and C terms, but this situation is rare in organic molecules.

SIGNS OF B TERMS FROM SEMIEMPIRICAL π-ELECTRON MODELS

Formula (2) can be used for numerical evaluation of B terms. In practice, the sums must be truncated, and origin-dependence of the magnetic moments then causes origin-dependence of the calculated B terms unless the molecule has high symmetry[3]. The finite basis set of AO's used in semiempirical models makes the summations finite, and if care is taken in the definition of the matrix elements of the model operators H (Hamiltonian), $\vec{R}$ (position) and $\vec{P}$ (linear momentum) so that $\left[H,\vec{R}\right] = i\hbar\vec{P}/m$ holds, the results of exact (full CI) calculations are origin-independent for molecules of any symmetry[4].

In the present survey, we shall concentrate on the signs of B terms of ππ* transitions of cyclic conjugated chromophores. These can be calculated using semiempirical models of various degrees of sophistication, but we shall use the simplest method which still provides reasonable predictions and physical insight. This is the simple version of the PPP model,[5] which is known to account for various other spectral properties of molecules of this kind. In recent years it has been shown to predict correct MCD signs for low-energy transitions in many of them, as well (for a list of references, see ref. 6). It is reassuring that these results are independent of the choice of parameters, extent of configuration interaction, and other details of the method[4]. Also, when only approximate solutions of the model is used, such as CI with singly excited configurations only, the results still show negligible origin dependence even for molecules of low

Downloaded At: 04:24 30 January 2011

symmetry[4]. A potentially serious deficiency of any π-electron theory of MCD spectra is its inherent inability to account for mixing of ππ* states with states involving excitations to or from orbitals of σ symmetry, such as nπ*. Fortunately, it appears that such mixing does not effect the signs of B terms of ππ* transitions decisively unless the contributions due to ππ*-ππ* mixing vanish or nearly vanish, which is rarely the case. In those molecules in which B terms of nπ* transitions in conjugated π-electron molecules have been measured, such as the aza derivatives of benzene[7] and naphthalene[8], quinones[9], etc., they are very small. It is quite possible, however, that the neglect of magnetic mixing of ππ*-σπ* type causes trouble at high energies, where simple PPP predictions frequently fail.

In addition to the numerous comparisons of calculated and experimental MCD signs reported by various authors and summarized in ref. 6, we now present a few additional comparisons of MCD sign sequences for the low-energy region in selected heterocycles:

benzofuran[10], thionaphthen[10], indole[11]: +-; calc.: +-
carbazole[10]: +-+-; calc.: +-+-
dibenzofuran[10]: +--+; calc.: +--+
dibenzothiophen[10], dibenzoselenophen[10]: +---; calc.: +--+
2-pyridone[12], 4-pyridone[12], 2-pyrimidone[12], 4-pyrimidone[12]: -+; calc.: -+
4-quinolone[13], 3-methyl-1-isoquinolone[13], 2-methyl-4-quinazolone[13], 2-methyl-4-quinolone[13]: -+-+; calc.: -+-+
4-methyl-2-quinolone[13], 3-methyl-2-quinoxalone[13]: --+-; calc.: ---+
4-hydroxy-2-quinolone[13]: +-+-; calc.: +--+

GENERAL RULES FOR MCD SIGNS OF LOW-ENERGY ππ* TRANSITIONS

While it is certainly of interest to note that the MCD signs of low-energy transitions can be calculated by the PPP model with a reasonable degree of reliability, even for fairly complicated heterocycles, this does

Downloaded At: 04:24 30 January 2011

not necessarily produce much physical understanding of the origin of these signs in terms of molecular structure. Fortunately, most frequently, very few contributions of the $B^{F}_{I,F}$ type are of importance for the low-energy B terms, and their signs can be deduced from mere inspection of the Hückel MO's of a suitable parent system[4]. Even better, with use of reasonable approximations it is possible to deduce general rules for MCD signs of low-energy transitions in cyclic π-systems, and these are likely to be of most importance for the non-specialist. The rest of this survey is devoted to the formulation and application of such general rules with emphasis on molecules somewhat simpler than the heterocycles just listed.

One rule which was first derived from theory[14], and since confirmed experimentally on several examples[15], predicts that the sign sequences for two species paired in the sense of alternant symmetry, such as benzyl cation and benzyl anion, should be mirror images of each other. A related consequence of the simple PPP model is the division of cyclic π-electron chromophores into soft (uncharged alternant hydrocarbons) and hard (charged alternant hydrocarbons and non-alternant hydrocarbons)[6]. The soft chromophores have no intrinsic sign pattern; rather, their MCD sign sequence is dominated by the nature and location of substituents and/or heteroatoms in an easily predictable way requiring a knowledge of the Hückel orbitals of the parent chromophore. The hard chromophores have an intrinsic sign pattern relatively difficult to perturb by substitution or introduction of heteroatoms. These results of the simple PPP model agree quite well with experiments[6].

Recently, a particularly general formulation of a rule for signs of low-energy B terms of conjugated cyclic compounds which can be related to an annulene containing 4N+2 electrons has been found[16]. It is based on the well known fact that many low-energy electronic states in these molecules

Downloaded At: 04:24 30 January 2011

can be, at least distantly, related to states of the perimeter (cf. the L_b, L_a, B_b, B_a notation of Platt[17]), and on the realization that the nodal properties of the perimeter orbitals, which are of decisive importance in determining MCD mixing signs, are not significantly changed upon even very drastic perturbations of the perimeter, such as cross-linking, introduction of conjugated bridges, substituents, and heteroatoms.

For annulenes, the MCD signs can be derived in closed form if a few reasonable approximations are introduced in the spirit of the classical work of Moffitt[18] (for more detail, see ref. 16). For a perturbed [n]-annulene with 4N+2 electrons ($n \geq 5$), four low-energy states result and the purely electronic contribution to the sign of the lowest-energy B term can be shown[19] to be given to a good approximation as

$$\text{sgn } B = \text{sgn } (\Delta\text{HOMO}-\Delta\text{LUMO}), \qquad (4)$$

where ΔHOMO is the separation of the highest occupied MO from the second highest occupied MO, and ΔLUMO is the separation of the lowest unoccupied MO from the second lowest unoccupied MO.

The general rule can now be specialized for a variety of more limited cases, and four examples follow.

a. Annulenes with 4N+2 Electrons.

Purely inductive (electron donating, -I; electron withdrawing, +I) perturbation leaves ΔHOMO = ΔLUMO to the first order, and small B terms are expected, in agreement with experimental results[7] for the azines. Second order perturbation theory predicts the correct signs for some of the azines (pyridine), but the magnitudes are very weak and in some instances mixing with nπ* states may then be non-negligible. Purely mesomeric perturbation causes ΔHOMO > ΔLUMO and positive lowest B term if it is electron donating (-

Downloaded At: 04:24 30 January 2011

and ΔHOMO < ΔLUMO and thus a negative lowest B term if it is electron withdrawing (+E). In the case of benzene, this again is in good agreement with experimental data[20]. Such simple arguments at the level of qualitative first and second order perturbation theory can also be used when several substituents are present. For instance, an inspection of the form of benzene orbitals shows that two like substituents reinforce each other's effect and do so more efficiently when they are in 1,4 positions than in 1,2 or 1,3 positions. Other cases of polysubstitution can be worked out similarly, and the combination of one I substituent and one E substituent is worked out in ref. 19 as an example. This particular case has been investigated on the aminopyridines and 2- and 3-fluoropyridines (lowest B term always positive) and the cyanopyridines (lowest B term negative in the 4-cyano isomer but positive in the 2 and 3 isomers), and excellent agreement with full PPP calculations and with experiment was found.[7,19]

Downloaded At: 04:24 30 January 2011

b. Highly Symmetrical Alternant Hydrocarbons (Degenerate HOMO and LUMO)

Simple considerations show that hydrocarbons such as triphenylene or coronene should behave like annulenes: I substituents have no effect to the first order, +E substituents yield negative lowest B terms, -E substituents positive lowest B terms. Experimental data are presently not available.

c. Uncharged Alternant Hydrocarbons (Soft Chromophores)

In these, ΔHOMO = ΔLUMO in the absence of further perturbation. Knowledge of the coefficients $C_{\mu,1}$ and $C_{\mu,2}$ for the highest two occupied MO's in the position of substitution μ then suffices for predictions. For the lowest B term, sgn B = sgn $(C^2_{\mu,1} - C^2_{\mu,2})$ if the substituent is of -I or -E type, and sgn B = sgn $(C^2_{\mu,2} - C^2_{\mu,1})$ if the substituent is of +I or +E type. Agreement with experiment is excellent although exceptions do exist[6].

d. Non-Alternant Hydrocarbons.

Inspection of Hückel MO energies provides correct sign predictions for the lowest B term in molecules such as azulene[21], benz[a]azulene[13], acenaphthylene[22], pleiadiene[23], fluoranthene[24], and many others.

Finally, the approximate nature of all results obtained in the simple approximation should be once more emphasized. Thus, the predictions are only for the effects of what are believed to be the generally dominant contributions, and in those cases in which these happen to vanish (ΔHOMO = ΔLUMO), the experimental B terms ought to be relatively small, but of unpredictable signs as far as the simplest approach is concerned.

In conclusion, it can be safely said that simple π electron theory allows formulation of quite powerful general rules for MCD signs of low-energy transitions in cyclic conjugated molecules. Thus, MCD is useful for the study of the electronic structure of such molecules and of the nature of substituent effects. It is conceivable that it will also find use as an auxiliary tool in structure elucidation, and it is already clear that it is much more powerful in this respect than ordinary U.V.-visible spectroscopy.

Downloaded At: 04:24 30 January 2011

ACKNOWLEDGEMENT

This work was supported by Public Health Service Grant No. GM 21153.

REFERENCES

1. Richard Merton Visiting Professor of the Deutsche Forschungsgemeinschaft, 1976. Permanent address: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

2. A. D. Buckingham and P. J. Stephens, Ann. Rev. Phys. Chem., 17, 399 (1966); P. N. Schatz and A. J. McCaffery, Quart. Rev., 23, 552 (1969).

3. L. Seamans and A. Moscowitz, J. Chem. Phys., 56, 1099 (1972); D. J. Caldwell and H. Eyring, J. Chem. Phys., 58, 1149 (1973).

4. S. M. Warnick and J. Michl, J. Am. Chem. Soc., 96, 6280 (1974).

5. R. Pariser and R. G. Parr, J. Chem. Phys., 21, 466, 767 (1953); J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).

6. J. Michl, Chem. Phys. Lett., 39, 386 (1976).

7. A. Castellan, D. Muller and J. Michl, unpublished results.

8. M. R. Whipple and J. Michl, unpublished results.

9. O. L. Acevedo and J. Michl, unpublished results.

10. M. A. Souto and J. Michl, unpublished results.

11. D. W. Miles and H. Eyring, Proc. Nat. Acad. Sci. USA, 70, 3754 (1973).

12. I. Jonáš and J. Michl, unpublished results.

13. A. D. Otteson and J. Michl, unpublished results.

14. J. Michl, J. Chem. Phys., 61, 4270 (1974).

15. R. E. Koning and P. J. Zandstra, Ber. Bunsenges. Phys. Chem., 80, 199 (1976); K. L. Tseng and J. Michl, J. Am. Chem. Soc., 98, 6138 (1976).

16. J. Michl, Chem. Phys. Lett., in press, and unpublished results.

17. J. R. Platt, J. Chem. Phys., 17, 484 (1949).

18. W. Moffitt, J. Chem. Phys., 22, 320, 1820 (1954).

19. J. Michl, Proceedings of the Nobel Workshop on Molecular Optical Dichroism and Chemical Applications of Polarized Spectroscopy, Lund, Sweden, 1976.

20. E.g., D. J. Shieh, S.-T. Lee, Y.-C. Yim, S. H. Lin, and H. Eyring, Proc. Nat. Acad. Sci. USA, 72, 452 (1975).

21. E. W. Thulstrup, P. L. Case and J. Michl, Chem. Phys., 6, 410 (1974).

22. E. W. Thulstrup and J. Michl, J. Am. Chem. Soc., 98, 4533 (1976).

23. J. Kolc and J. Michl, J. Am. Chem. Soc., 98, 4540 (1976).

24. J. Kolc, E. W. Thulstrup, and J. Michl, J. Am. Chem. Soc., 96, 7188 (1974).

Downloaded At: 04:24 30 January 2011