

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 15.¹ Benzazulenes

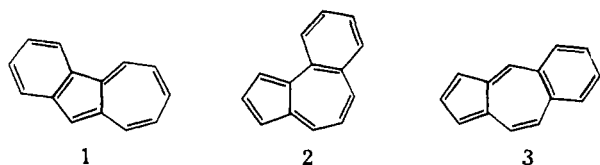
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Abstract. Magnetic circular dichroism of benz[*a*]azulene and benz[*f*]azulene is reported and interpreted in terms of the simple theory of parts 1–3, requiring no computations. Excellent agreement is found for the lowest three transitions in these positive-hard MCD chromophores and quite different MCD signs are predicted for the negative-hard isomer benz[*e*]azulene which has not been measured so far.

Introduction

The three benzazulenes 1–3 can be formally derived from [14]annulene by introduction of two cross-links, one between two atoms of like kind (both starred, even perturbation), and the other between two atoms of different kinds (one starred, the other unstarred, odd perturbation). Thus, even in the crudest approximation, all symmetries relating the frontier orbitals of the annulene, *s*, *a*, $-s$, $-a$ (in the notation of parts 1–3³), should disappear. Therefore, $\Delta\text{HOMO} \neq \Delta\text{LUMO}$,



except by accident, and, barring such an accident, hydrocarbons such as these should generally belong to the class of hard MCD chromophores (ΔHOMO and ΔLUMO are defined in terms of orbital energies: $\Delta\text{HOMO} = |E(\mathbf{a}) - E(\mathbf{s})|$, $\Delta\text{LUMO} = |E(-\mathbf{a}) - E(-\mathbf{s})|$). Inspection of tables of Hückel orbital energies shows that 2 is a negative-hard chromophore (ΔHOMO is smaller), while 1 and 3 are positive-hard (ΔLUMO is smaller). However, the difference $\Delta\text{HOMO} - \Delta\text{LUMO}$ is small in the case of 3, which should thus represent an intermediate case between a positive-hard and zero-soft chromophore. In the present paper, we report PPP calculations by the standard simple method without adjustment for MCD purposes for 1–3 and experimental results for 1 and 3. The rather striking theoretical prediction for 2 is allowed to stand for future verification.

The absorption spectra of the benzazulenes have been reported,⁴ as has a series of increasingly more sophisticated π -electron calculations.^{5,6} For our purposes, the identification of the four L and B bands based on consideration of the absorption spectra and a theoretical analysis using the perimeter model⁶ is of particular importance: L_1 near 17 000 cm^{-1} , L_2 near 25 000 cm^{-1} , B_1 near 31 000 cm^{-1} , B_2 near 34 000 cm^{-1} .

Experimental Section and Calculations

The synthesis of 1 and 3 has been reported.⁷ They were purified by gradient sublimation. The measurements and calculations were performed as in part 4.⁸

Results

The experimental results are shown and compared with calculations in Figures 1 and 2. The calculations are of the standard PPP type which incorporates only nearest-neighbor effects. From the general theory of parts 1–3,³ one can expect

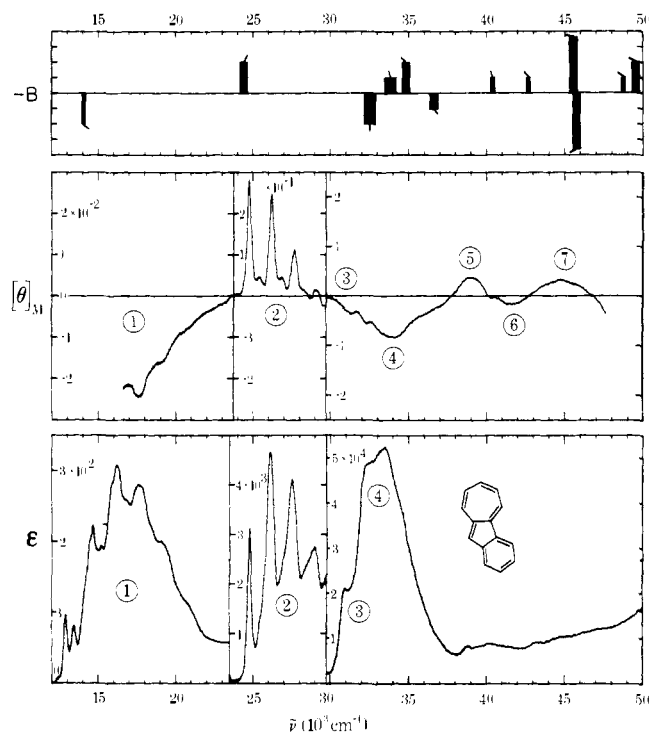


Figure 1. Benz[*a*]azulene: bottom, absorption; center, MCD; top, calculated transitions represented by bars (thin, oscillator strength $f \leq 0.1$; medium, $0.1 < f \leq 0.5$; thick, $f > 0.5$). The direction and length of the bar indicate the sign and magnitude of the *B* term. The flags give the polarization direction with respect to the formula shown.

for a [14]annulene perimeter additional contributions from next-nearest-neighbor terms, as discussed below. While more sophisticated calculations incorporating these can be envisaged readily, our main present purpose is a qualitative discussion of general trends, and a secondary purpose is an evaluation of the performance of the standard PPP model.

The figures show a proposed analysis of the spectra in terms of individual electronic transitions, numbered sequentially. The identifications $L_b = L_1 = 1$, $L_a = L_2 = 2$, $B_1 = 3$, and $B_2 = 4$ are standard.⁶ The MCD spectrum shows that the absorption band of 3 at 35 000 is composed of at least two transitions, labeled 4 and 5, and one wonders whether the same is not true in 1. Several higher transitions are clearly present in the MCD (but not absorption) spectra, but no claim is made presently about their exact number and nature. Certainly, calculations suggest congestion sets in somewhere near the two B transitions. Application of the simple theory of part 2³ yields the following results.

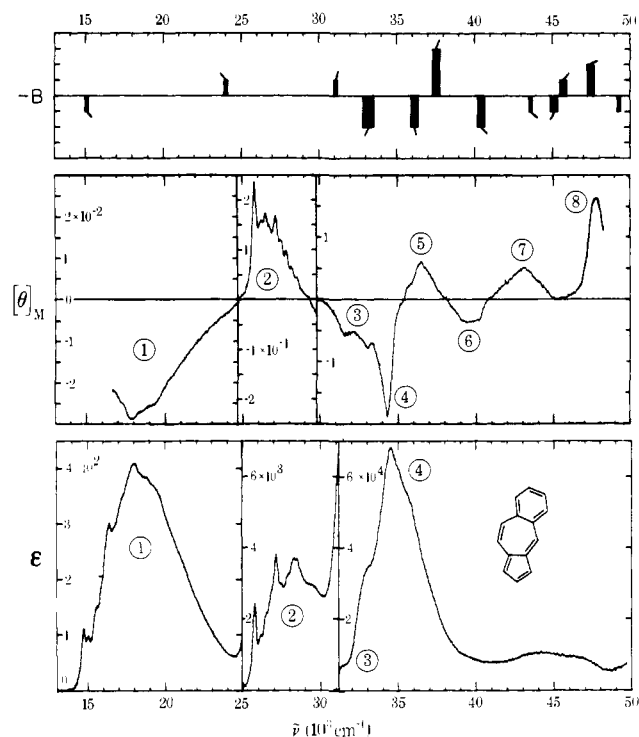


Figure 2. Benz[7]azulene. See caption to Figure 1.

The μ^- contribution, which is inherent to all [14]annulene perimeters but relatively small, provides a small positive contribution to $B(L_1)$ due to both L_1-L_2 and L_1-B_2 mixing, a small positive contribution to $B(L_2)$ composed from a positive term due to B_1-L_2 mixing and a smaller negative term due to L_2-L_1 mixing, and larger contributions to $B(B_1)$ and $B(B_2)$ dominated by their mutual mixing, the former positive and the latter negative. To this must now be added the μ^+ part which is potentially much larger but enters multiplied by a factor which depends on the $\Delta HOMO - \Delta LUMO$ difference. As soon as $\Delta HOMO \neq \Delta LUMO$, this part should dominate at least the MCD of the L bands, where the μ^- contributions are small.

In **1** and **3**, $\Delta HOMO > \Delta LUMO$, and the formulas predict positive μ^+ contributions to $B(L_1)$ and to $B(B_1)$ and negative contributions to $B(L_2)$ and $B(B_2)$. Adding both parts, we then expect $B(L_1) > 0$, $B(L_2) < 0$, $B(B_1) > 0$, and $B(B_2) < 0$. This agrees with the experimental results (Figures 1 and 2) except for B_2 . The probable source for the discrepancy is the presence of several additional states very close to B_2 which are not considered in the simple theory.

In **2**, where $\Delta HOMO < \Delta LUMO$, the μ^+ part is expected to contribute negative amounts to $B(L_1)$ and $B(B_1)$ and positive amounts to $B(L_2)$ and $B(B_2)$. Now, adding both parts is without problems for the L_2 band and $B(L_2) > 0$ can be predicted confidently. Also, a negative or at most very weakly positive $B(L_1)$ is certain. On the other hand, it is impossible to predict the signs of the B bands with confidence from the simple theory, particularly in view of the expected presence of additional transitions in this region.

The prediction of $B(L_1) < 0$ and $B(L_2) > 0$ is quite intriguing, since so far all azulenes whose MCD has been measured have had $B(L_1) > 0$ and $B(L_2) \leq 0$. These include azulene itself,⁹ alkylazulenes,¹ two isomeric azulenophenalenenes,¹⁰ and the two benzazulenes reported presently. But then, for all

of these, $\Delta HOMO > \Delta LUMO$, while for **2**, $\Delta HOMO < \Delta LUMO$ is calculated. A measurement on **2** will provide an interesting test of the predictive power of the simple theory developed in parts 1-3.³

The variation of the MCD signs of azulene with benzoannulation is related to its "almost soft" nature¹ in the transition region between soft and hard chromophores. As shown in parts 17¹¹ and 18¹² and ref 13, benzoannulation in "truly hard" chromophores such as acenaphthylene or pleiadiene has no such effect. In their turn, **1** and **2** are expected to be very hard chromophores since their $\Delta HOMO$ is quite different from $\Delta LUMO$, whereas **3** is predicted to be intermediate between positive-hard and zero-soft, and its MCD signs could be changed by strong substitution (the $\Delta HOMO - \Delta LUMO$ difference is small).

Comparison of the experimental results with the full PPP calculations by the standard method which incorporates only nearest-neighbor effects brings little over the use of the simple theory for the lowest few transitions but shows clearly the expected congestion in the region of 35 000 cm^{-1} and above. While it is possible to assign many of the calculated transitions to experimental ones so as to make the MCD signs agree, we doubt the physical meaningfulness of such a procedure. Here, measurements of additional properties such as polarization directions might help.

Conclusions

In addition to showing the presence of new transitions in **1** and **3**, their MCD spectra serve to further verify the simple theory of parts 1-3.³ In both compounds, MCD signs follow the pattern well-known from other azulene analogs. The same simple theory predicts quite different signs for **2**, particularly for its L_2 band.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 21153. We thank Dr. Henry Eyring, University of Utah, for kind permission to use his MCD instrument. Helium gas was provided through a departmental grant from the Office of Naval Research.

References and Notes

- (1) Part 14: W. Gerhartz and J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (2) (a) University of Utah; (b) Technische Hochschule, Munich.
- (3) J. Michl, *J. Am. Chem. Soc.*, companion papers in this issue (parts 1-3).
- (4) P. A. Plattner, A. Fürst, and W. Keller, *Helv. Chim. Acta*, **32**, 2464-2474 (1949); J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825-831 (1949); E. Kloster-Jensen, E. Kováts, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 1051-1067 (1956); W. Ziegenbein and W. Treibs, *Justus Liebigs Ann. Chem.*, **595**, 211-218 (1955).
- (5) G. Berthier, B. Pullman, and J. Baudet, *J. Chim. Phys. Phys.-Chim. Biol.*, **50**, 209-214 (1953); H. Götz and E. Heilbronner, *Helv. Chim. Acta*, **44**, 1365-1373 (1961); J. Koutecký, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439-2456 (1964); N. Tyutyulkov and F. Fratev, *Theor. Chim. Acta*, **5**, 376-378 (1966); G. Tröger and J. Fabian, *Z. Phys. Chem. (Leipzig)*, **247**, 139-150 (1971).
- (6) E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1-18 (1963).
- (7) C. Jutz and E. Schweiger, *Chem. Ber.*, **107**, 2383-2396 (1974).
- (8) A. Castellán and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
- (9) E. W. Thulstrup, P. L. Case, and J. Michl, *Chem. Phys.*, **6**, 410-418 (1974); H. P. J. M. Dekkers and S. W. T. Westra, *Mol. Phys.*, **30**, 1795-1811 (1975); A. Tajiri and M. Hatano, *Chem. Phys. Lett.*, **34**, 29-33 (1975).
- (10) E. W. Thulstrup, J. Michl, and C. Jutz, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1618-1628 (1975); A. Tajiri, M. Hatano, I. Murata, and K. Nakasuji, *Chem. Lett.*, 543-546 (1976).
- (11) G. P. Dalgaard and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 17).
- (12) M. A. Souto, D. Otteson, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 18).
- (13) J. Michl and J. F. Muller, *J. Am. Chem. Soc.*, **98**, 4550-4553 (1976).