Magnetic Circular Dichroism Studies. V.[1] Ivestigation of Some Cyclodecapentaene Derivatives[2]

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Abstract: Magnetic circular dichroism spectra (MCD) are reported for some bridged [10]annulenes; all absorption bands down to 230 nm were investigated. A qualitative theoretical treatment of the results is attempted on the basis of our previous work on other annulene systems. The relationship between the sign of MCD values and the polarization of the corresponding band in the absorption spectra is discussed and solvent effects are shown experimentally. Especially interesting results are obtained with 1,6-imino- and 1,6-oxy-bridged compounds, which suggest interactions of the nonbonding nitrogen or oxygen electrons with the ten-π-electron system of the ring.

Utilization of magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD) as spectroscopic tools has been delayed until this decade because of the previous lack of adequate intrumentation and theoretical understanding of the results. However, the present availability of highly sensitive photoelectric spectropolarimeters coupled with new theoretical developments[5] has greatly spurred interest in this field.

The advantages of MCD over MORD measurements have already been emphasized[6] and the results have been shown to be quite valuable in determining the nature of excited states of ions and molecules.[7] In certain cases the magnetic moment of the excited state, if present, can also be determined from these results. At the other extreme, MORD spectra have been shown to be useful for following the kinetics of a biochemical redox reaction,[8] thus showing that the technique is of analytical as well as theoretical interest.

In addition, our interest has centered on the use of MCD spectra as a tool for deriving structural information about organic molecules. Previous encouraging results from our laboratory[9] indicate that MCD is far more sensitive to the influence of various external substituents on the chlorin chromophore than the more usual techniques of absorption spectroscopy and natural circular dichroism.

The compounds[10] whose MCD spectra are reported in this paper were of interest for two reasons. First, as [10]annulenes, they extend the number of annulene systems we have studied.[1] But more significantly, since several compounds were available with the same framework but different substituents, this series constituted another test of the sensitivity of MCD spectra to structural variations.

Experimental Section

The instrumentation involved in our MCD measurements has already been discussed,[6] but important modifications have been made to the system that should be stressed. The two Lockheed superconducting magnets[11] previously used[12] have been replaced by our own Lockheed superconducting magnet (Model OSCM-103) with design changes which increase its convenience for our particular use. These consist of a larger dewar, thereby necessitating only daily filling, and walls of increased thickness which reduce the compression of the insulation and thereby result in more efficient use of liquid helium. The magnetic field employed is again 50 kG.

The results are reported in terms of molar magnetic ellipticity ($[\theta]_M$ in deg G^{-1} mol^{-1} cm^2), meaning that the spectra are again normalized to 1 G, as in our last paper[1] but contrary to our earlier work.[6,9] However, the same sign convention used throughout our previous work is employed. On each figure the error in MCD amplitude was estimated and indicated by a barred line. The double barred line shown on the left part of the spectra indicates a change in the concentration required to perform the measurements—the error thus being different in the two sections. All compounds are given in Table I, their structures being reproduced on the figures.

With the exception of 1,6-iminocyclodecapentaene (I), all molecules were fairly stable crystalline solids and were used without further purification. 1,6-Iminocyclodecapentaene was purified by vacuum distillation at 0.1 torr and the spectrum measured soon after purification. All compounds were measured in spectrograde methanol. In addition, some experiments (see Table I) were performed in cyclohexane or in acid medium in order to investigate possible solvent effects. Both absorption (Cary 14 spectrophotometer) and MCD measurements were carried out at room temperature. Unless otherwise stated, the acid medium was obtained by adding 2 drops of 12 *N* hydrochloric acid to 10 ml of methanol.

Theoretical Remarks

1. Absorption Spectra.

Compounds I–IV have been the object of a recent experimental and theo-

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(1) Paper IV: B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 7062 (1967).

(2) We are indebted to the National Science Foundation (Grant No. GP-7432) and to the National Institutes of Health (Grant No. GM-12173) for financial aid.

(3) Recipient of a NATO postdoctoral fellowship (1966–1967) and a Fulbright travel grant while on leave from the Laboratoire d'Optique Physique, E.S.P.C.I., Paris 5ᵉ, France.

(4) National Science Foundation Predoctoral Fellow, 1963–1966.

(5) For a recent review, see A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

(6) D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Nat. Acad. Sci. U. S.*, **56**, 1377 (1966); see also B. Briat and C. Djerassi, *Nature*, **217**, 918 (1968).

(7) For leading citations, see ref 1 and 9.

(8) V. E. Shashoua, *Arch. Biochem. Biophys.*, **111**, 550 (1965).

(9) B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 6170 (1967).

(10) E. Vogel, W. Pretzer, and W. A. Böll, *Tetrahedron Lett.*, 3613 (1965); F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, **86**, 3168 (1964); E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem. Intern. Ed. Engl.*, **3**, 642 (1964); E. Vogel and H. D. Roth, *ibid.*, **3**, 228 (1964); E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965); E. Vogel, Special Publication No. 21, The Chemical Society, London, 1967, p 113; W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 354 (1965).

(11) S. R. Hawkins and J. H. Harshman, *Rev. Sci. Instr.*, **38**, 50 (1967).

(12) We are grateful to Professor R. L. White of the Departments of Electrical Engineering and Material Science, Stanford University, and to Lockheed Research Laboratories (Palo Alto) for the use of their superconducting magnets at various times during our investigations.

Table I. List of Compounds

Name	Figure
1,6-Iminocyclodecapentaene (I)	1a (MeOH) 1b (cyclohexane) 1c (MeOH + H$^+$)
1,6-Oxycyclodecapentaene (II)	2a (MeOH) 2b (cyclohexane)
N-Methyl-1,6-iminocyclodecapentaene (III)	3a (MeOH) 3b (cyclohexane)
1,6-Methanocyclodecapentaene (IV)	4a (MeOH) 4b (cyclohexane)
11-Bromo-1,6-methanocyclodecapentaene (V)	5 (MeOH)
2,10-Dibromo-1,6-methanocyclodecapentaene (VI)	6 (MeOH)
2,7-Dibromo-1,6-methanocyclodecapentaene (VII)	7 (MeOH)
N-Acetyl-1,6-iminocyclodecapentaene (VIII)	8 (MeOH)
1,6-Methanocycloundecapentaenyl fluoroborate (IX)	9 (MeOH)

retical spectroscopic study.[13] The basic features of their absorption spectra (in cyclohexane) were interpreted by means of Platt's[14] perimeter model for cyclic π-electron systems. Electronic transitions are explained in terms of the promotion of a π electron from the two highest filled orbitals to the two lowest empty ones. The over-all ground-state configuration, $\Gamma = (d)^2(e)^4(f)^4$, is totally symmetric (^1A), this arising from the pairing properties of electrons in orbitals. In the approximation of the D_{10h} point group, the excited states are B_{2u}, B_{1u}, and E_{1u}, the latter being degenerate. When the symmetry is reduced to D_{2h} (first approximation), the degeneracy is removed and one obtains four nondegenerate excited states of symmetry B_{2u}, B_{3u}, B_{2u}, B_{3u}.[13] Four absorption bands are therefore predicted (^1L_b, ^1L_a, ^1B_b, and ^1B_a in Platt's nomenclature). With the previously adopted[13] axis convention (y axis parallel to the long axis of the molecule and z axis perpendicular to the plane of the molecule), ^1L_a and ^1B_a are x polarized while ^1L_b and ^1B_b are y polarized. The L bands are "momentum forbidden" and have therefore a weak intensity, whereas the B bands are "momentum allowed" and are much stronger. Finally, it is worth noting that the ^1L_b band was always encountered at longer wavelength in the compounds[13] under consideration.

2. **Qualitative Prediction of MCD Spectra.** When both the ground and excited states of a molecule are nondegenerate, theory[5] predicts only B terms in MCD spectra (see ref 1 and 9 for nomenclature and the sign convention adopted), *i.e.*, the dispersion of MCD as a function of wavelength through an absorption band has a characteristic bell shape and looks like an ordinary absorption curve. As shown earlier,[1] the B parameter (or actually the ratio of the B parameter to the dipole strength D of the band) can be extracted simply from the experimental data. This is of no use for our purpose here since we will be dealing with the sign of B only.

In the case of an isolated transition and for a molecule possessing nondegenerate states, the quantum mechanical expression for B and D is[15,16]

$$B_{\mathrm{oa}} = I_m\left\{\sum_{\mathrm{b}\neq 0}\frac{m_{\mathrm{bo}}}{\nu_{\mathrm{bo}}}\cdot\mu_{\mathrm{oa}} \times \mu_{\mathrm{ab}} + \sum_{\mathrm{b}\neq \mathrm{a}}\frac{m_{\mathrm{ab}}}{\nu_{\mathrm{ab}}}\cdot\mu_{\mathrm{oa}} \times \mu_{\mathrm{bo}}\right\} \tag{1}$$

$$D_{\mathrm{oa}} = \mu_{\mathrm{oa}}{}^2 \tag{2}$$

where μ and m are the electric and magnetic dipole transition moments, respectively. The subscripts o, a, b designate the ground and two excited electronic states, whereas I_m indicates taking the imaginary part of the bracketed expression in eq 1; ν_{bo} and ν_{ab} stand for the energy difference between states o–a and a–b. An examination of the character table for the D_{2h} point group[17] shows that the first term in B_{oa} is symmetry forbidden, while the second one is symmetry allowed. The expression for B_{oa} then reduces to

$$B_{\mathrm{oa}} = Im\sum_{\mathrm{b}\neq \mathrm{a}}\frac{m_{\mathrm{ab}}}{\nu_{\mathrm{ab}}}\mu_{\mathrm{oa}}\mu_{\mathrm{bo}} \tag{3}$$

For pure D_{2h} symmetry, there exist μ_{oa} and μ_{ob} vectors which are directed along the two perpendicular axes in the plane of the molecule, whereas m_{ab} is directed along the z axis. The absolute value of the triple cross vectorial product therefore reduces simply to the product of the lengths of the three vectors and B_{oa} is expected to have a relatively large value.[18] If this symmetry is assumed as a first approximation, in the [10]annulenes, a B_{2u} state can only be magnetically coupled to a B_{3u} state and *vice versa*, while they are both electrically coupled to the ground state with perpendicular polarizations in the molecular plane.

Equations 2 and 3 lead to a number of predictions. First, in contrast to the dipole strength D, B may be either positive or negative,[19] depending upon the relative orientation of m_{ab}, μ_{oa}, and μ_{bo}. Second, if only two excited states are coupled by the magnetic field, B_{oa} and B_{ob} will have equal magnitude but opposite signs. This was the simplification adopted by Pershan, *et al.*[20] On the other hand, if the coupling between two B_{3u} and one B_{2u} states (and *vice versa*) is considered, B_{oa} will be the sum of two terms, each being weighted according to the inverse of the frequency difference between the B_{2u} and the B_{3u} states, and B terms of *opposite sign* but *unequal magnitude* will be observed.

It is also clear from eq 3 that the sign of B_{oa} greatly depends upon the *relative* polarization of the electronic transitions o → a and o → b. It can be shown however that B_{oa} does not respond to the *absolute* polarization of o → a. Suppose that only two excited states are considered and let us assume first that o → a is y polarized (*i.e.*, μ_{oa} is directed along the long axis of the molecule). B_{oa} then becomes

$$B_{\mathrm{o}y} \sim I_m m_{yx}\cdot\mu_{\mathrm{o}y} \times \mu_{x\mathrm{o}}$$

If the same component is now x polarized, one has

$$B_{\mathrm{o}x} \sim I_m m_{xy}\cdot\mu_{\mathrm{o}x} \times \mu_{y\mathrm{o}}$$

Since the magnetic and electric moment operators are

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[13] H. R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J. P. Weber, *Helv. Chim. Acta*, **49**, 2017 (1966).

[14] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[15] P. J. Stephens, W. Suetaka, and P. N. Schatz, *ibid.*, **44**, 4592 (1966).

[16] As shown in ref 15, a proportionality factor should actually be included in the expressions of B and D to give an account of the modification of the electric field of the light wave by the medium. As the same factor enters into both terms, it is convenient to use the ratio $B:D$ for extracting the molecular parameters of interest.

[17] See, for example, L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

[18] A. Moscowitz, *Proc. Roy. Soc.* (London), **A297**, 16 (1967).

[19] I. Tinoco, Jr., and A. Bush, *Biopolymers Symp.*, **1**, 235 (1964).

[20] P. S. Pershan, M. Gouterman, and R. L. Fulton, *Mol. Phys.*, **10**, 397 (1966).

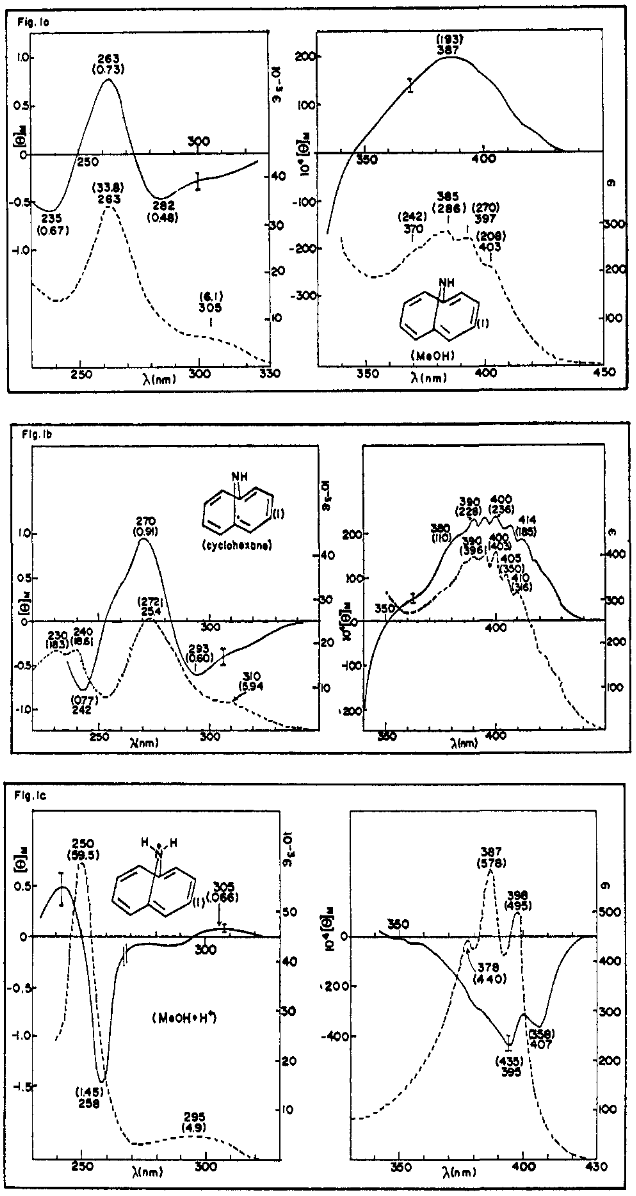

Figure 1. Absorption (- - -) and MCD (——) of 1,6-iminocyclodecapentaene (I): (a) in MeOH; (b) in cyclohexane; and (c) in MeOH + H⁺.

Hermitian and the basis function can be taken as real, only m_{yx} (or m_{xy}) is imaginary and

$$I_m m_{yx} = -I_m m_{xy}$$

$$\mu_{oy} = \mu_{yo}$$

$$\mu_{ox} = \mu_{xo}$$

It follows that $B_{ox} = B_{oy}$ since the first vectors m are directed along two opposite directions while the others, although of equal length, are considered in the reverse order in the triple cross vectorial product. Our conclusion is thus similar to that of Stephens, *et al.*,[15] who show that the qualitative form of the MORD spectrum was independent of the order of the Q bands in the free bases of the porphyrin and phthalocyanine series.

As stated earlier,[5] the above arguments are valid only for an electronically allowed transition or an electronically forbidden transition which is vibrationally allowed by a *single vibration* and where the absorption band consists of a totally symmetric vibrational progression superimposed on a single quantum in this vibration. In this latter situation (case I), B terms should have the same shape for every vibronic component, varying in magnitude in the same way as the vibronic components of the absorption band. On the other hand (case II), if the absorption band is vibrationally allowed by many vibrations of different symmetries,[21] many B terms of the same or opposite signs will be observed in the MCD spectrum through the absorption band.[9]

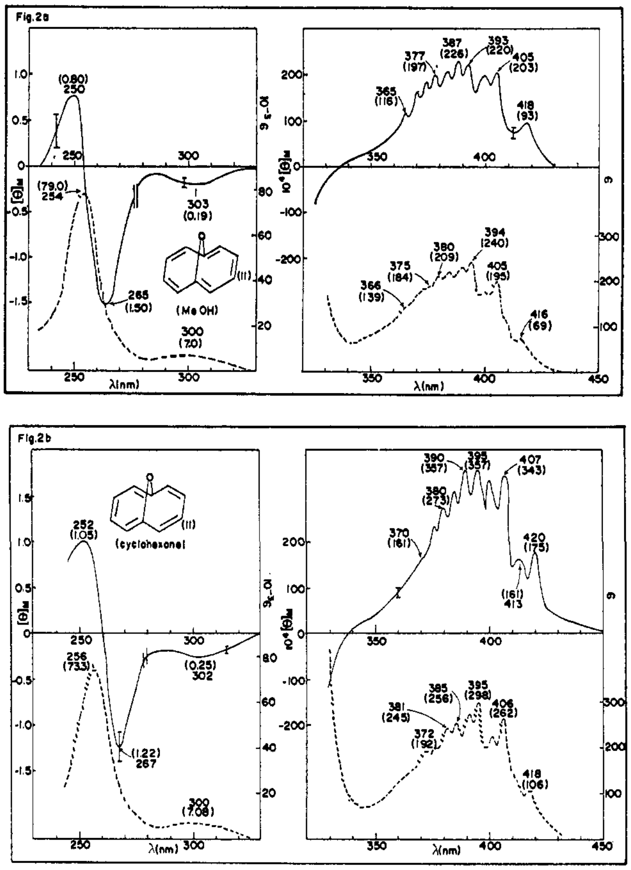

Figure 2. Absorption (- - -) and MCD (——) of 1,6-oxycyclodecapentaene (II): (a) in MeOH; (b) in cyclohexane.

Discussion of Results

Before discussing in detail the various MCD spectra, attention should be paid to the following observations. The absorption spectra of all molecules in methanol present the same basic features and reveal only three bands, the one located around 400 nm showing a vibrational pattern. It so happens that the two theoretically predicted B bands (near 260 nm) are not well resolved in this solvent nor in a nonpolar solvent like cyclohexane (compare Figure 1a and 1b or 2a and 2b, for example). On the other hand, MCD spectra reveal unambiguously two B terms of opposite sign through the 250–290-nm range and clearly demonstrate the presence of two absorption bands. However, these opposite B terms always have unequal magnitude (see Figure 3, for example) and mutual magnetic interaction between more than two states should be considered if a quantitative fit is attempted. More complicated fea-

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[21] See, for example, R. M. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, Inc., New York, N. Y., 1966, p 234.

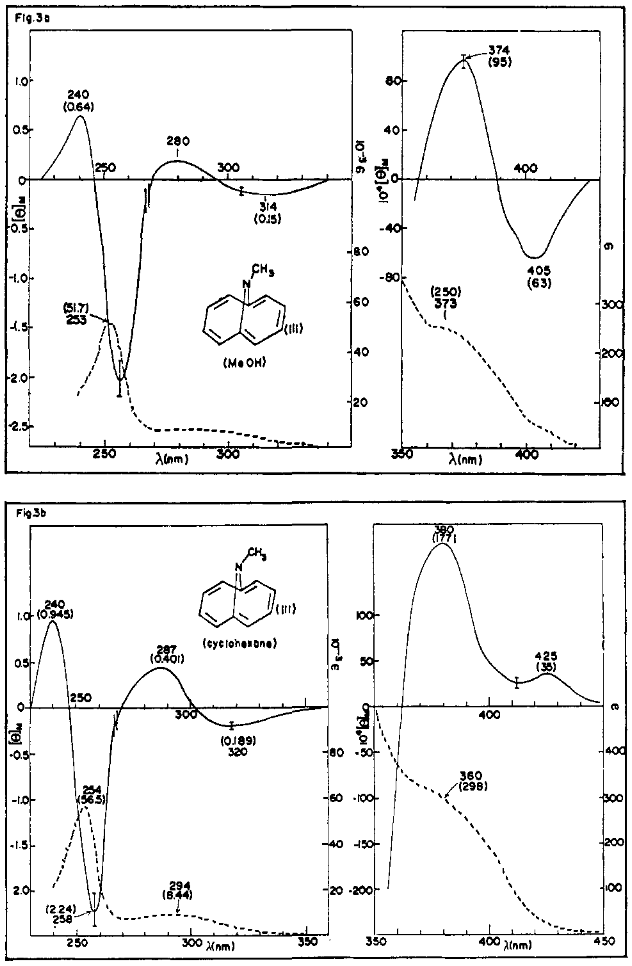

Figure 3. Absorption (- - -) and MCD (——) of N-methyl-1,6-iminocyclodecapentaene (III): (a) in MeOH; (b) in cyclohexane.

tures are associated with the ^1L_b band at longer wavelength (360–420-nm range) and will be discussed more completely in the following section. The situation through the ^1L_b band (around 300 nm) is rather complex in all curves. In order to fit even approximately the experimental results (a positive and a negative lobe in Figure 3a, for example), we must invoke either vibrational components of different symmetry (case II above) or an additional absorption band between ^1L_a and $^1B_{a,b}$. The latter seems more likely in view of the absorption spectra, and this tends to support the hypothesis of the possible existence of this band.[13,22]

For convenience, the samples have been classified into four groups, the grouping being based on the close resemblance within the group of their MCD spectra through the absorption band located at longer wavelength.

A. **Group 1 (Figures 1 and 2)** includes the imino (I) and oxy (II) compounds. Polarization measurements[13] show the order of the bands to be ^1L_b, ^1L_a, ^1B_a, ^1B_b with decreasing wavelength (respective polarizations y, x, x, y). It is interesting to correlate these polarizations with the +, —, —, + sign alternation observed in the MCD spectrum of II (see Figure 2a). The same correlation would hold for compound I (Figure 1a) if the MCD peaks at 282 and 263 nm were ascribed to the ^1B_a and ^1B_b bands, respectively. The splitting of the two B absorption components for compound I would then probably be larger than for compound II since the peak-to-peak MCD amplitude in Figure 1a is reduced as compared to that in Figure 2a (see eq 3). Both spectra have also been run in cyclohexane (Figures 1b and 2b). The pattern is the same, although both the absorption and MCD spectra are better resolved in the region of the ^1L_b band and the magnitudes are somewhat different from those observed in methanol. Finally, an additional absorption component was reported[13] at 239 nm for compound I in cyclohexane (see Figure 1b) with a polarization similar to that of the ^1B_b component. The sign of the observed MCD peak is unfortunately of no use in testing this assumption on a qualitative basis.

It seemed to us of interest to observe the effect of the protonation of NH or O. This was done apparently successfully for the imino compound I by use of a few drops of concentrated hydrochloric acid in methanol (Figure 1c). Drastic changes resulted in the MCD spectrum, the B term located at higher wavelength being now inverted as compared to the situation in pure methanol. On the other hand the alternation −, +, −, + is now observed for the respective signs of the MCD terms concerned, the curve being thus similar to those in group 3 (see below). Substitution of a few drops of commercial boron trifluoride etherate for the concentrated hydrochloric acid gave virtually the same result, although the magnitudes are somewhat altered (*i.e.*, $[\theta]_M$ maximum goes from −435 to −586 for the ^1L_b band in I). Acidification (with a few drops of perchloric acid or boron trifluoride etherate) of the less basic oxygen compound II resulted only in changes in magnitude ($[\theta]_M$ goes from +226 to +302 in MeOH and MeOH + $HClO_4$, respectively). It should be pointed out that, in contrast to the case of the above imino compound, this experiment may well be criticized since in 1,6-oxido[10]annulene, proton attack at the carbons—inducing rearrangement—can possibly compete with protonation on oxygen, and also protonation of solvent is as likely as protonation of II.

Comparison of Figures 2a and 2b shows that the MCD terms of opposite signs are more or less dissymmetric according to the solvent throughout the range where the B bands occur. An explanation can possibly be offered in terms of mixing of the B states with the appropriate L states. It should also be kept in mind that the results are relatively inaccurate in this region as far as the magnitudes are concerned, due to the weakness of the measured ellipticities.

B. **Group 2 (Figures 3 and 4).** The MCD spectra of these two molecules through the ^1L_b band (340–420 nm) in methanol (Figures 3a and 4a) is very different from that of compounds I and II, showing here a large number of B terms, the B values ranging from positive on the red side of the band to negative on the blue side. As suggested earlier in this paper (case II in the previous section), this seems to indicate that the band is vibrationally allowed by many vibrations of different symmetries, thus changing the polarizations and the sign of the B terms. If this is true, a solvent effect could possibly be expected. This is clearly the case in Figures 3a and 3b where two lobes of opposite sign are observed in methanol, the two lobes being of the same sign in cyclohexane. Actually it should be pointed out

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[22] E. Heilbronner, private communication.

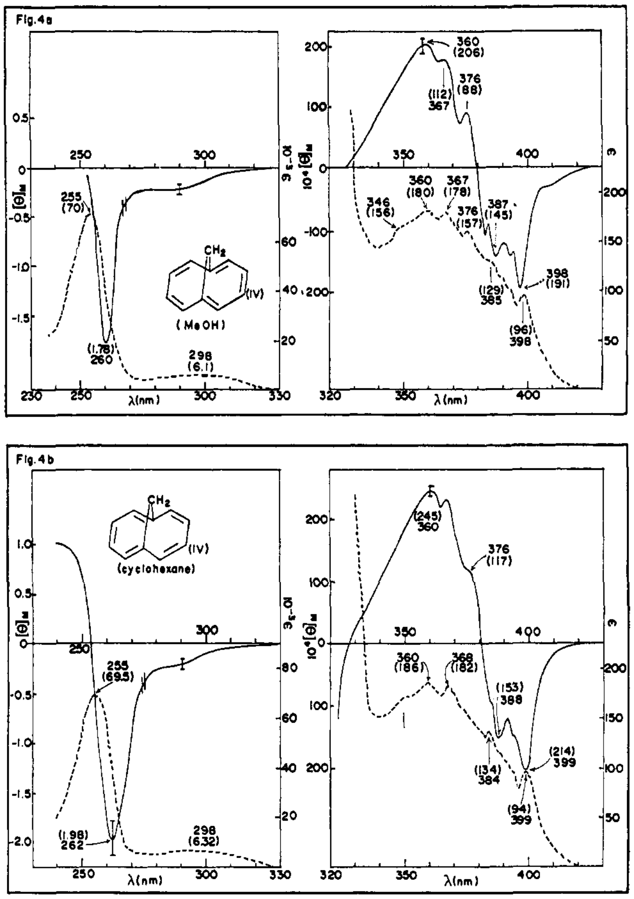

Figure 4. Absorption (- - -) and MCD (——) of 1,6-methanocyclodecapentaene (IV): (a) in MeOH; (b) in cyclohexane.

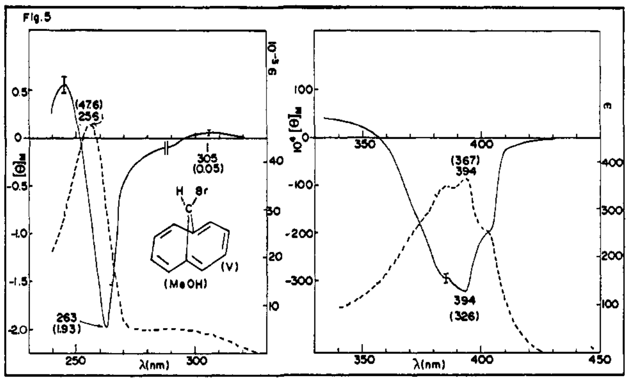

Figure 5. Absorption (- - -) and MCD (——) of 11-bromo-1,6-methanocyclodecapentaene (V) in MeOH.

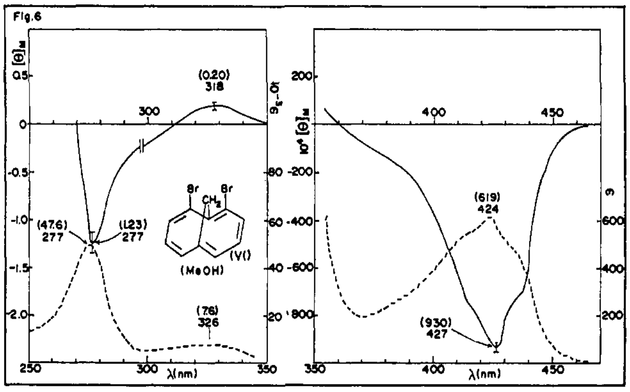

Figure 6. Absorption (- - -) and MCD (——) of 2,10-dibromo-1,6-methanocyclodecapentaene (VI) in MeOH.

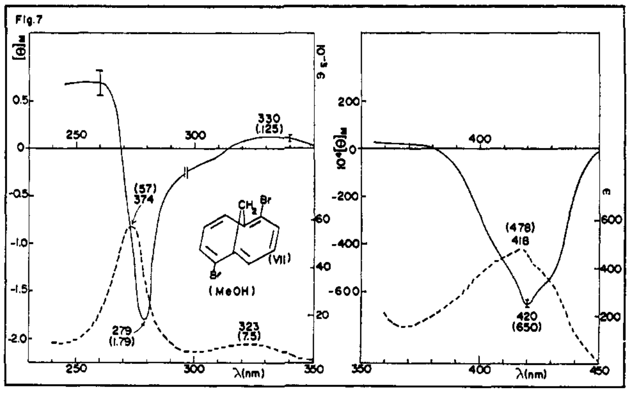

Figure 7. Absorption (- - -) and MCD (——) of 2,7-dibromo-1,6-methanocyclodecapentaene (VII) in MeOH.

here that MCD is by far more sensitive than absorption in revealing vibrational processes. 1,6-Methanocyclodecapentaene (IV) was also measured in cyclohexane (Figure 4b) but only the magnitudes of the two lobes are affected, their sign being unchanged. The following explanation can be advanced. Values of $[\theta]_M$ for the N-methylimino compound III through the ^1L_b band are smaller (about two to three times) than for the methano analog IV, which suggests that MCD is more forbidden for the former. It is then suggested—as often found in absorption spectroscopy—that the solvent can partly remove this forbiddenness.

The absorption spectra of the two compounds in cyclohexane have recently been classified[13] as showing the progression ^1L_b, ^1L_a, ^1B_b, and ^1B_a (with polarizations y, x, y, x) as far as the relative energy of the excited states is concerned. This order cannot be inferred from our MCD results and no correlation is even possible since the MCD spectrum through the ^1L_b bands does not have a definite sign. It is also worth pointing out that the MCD spectrum of the N-methyl compound III (see Figure 3a) reveals two *B* terms at 280 and 314 nm. This would tend to support the existence of an additional absorption band due to the lone pair of electrons on the nitrogen.

C. **Group 3 (Figures 5–8).** The details of the absorption spectra of these molecules have not yet been discussed in the literature, although the same basic features might be expected as for others. In particular, the order of the levels should be "normal," *i.e.*, an alternation of b and a bands (or y and x polarizations). Considering Figure 8 as an example, it is interesting to note that the sign of the $[\theta]_M$ maximum values also alternates for the peaks located around 237, 257, and 310 nm, and in the 400-nm region.

The characteristics of the MCD spectrum through the band at longer wavelength should be emphasized. Here $[\theta]_M$ is negative (in contrast to what is observed in group 1) and the MCD spectrum looks like the mirror image of the absorption spectrum, shoulders occurring at about the same wavelengths in both of them and $[\theta]_M$ being sensibly proportional to the maximum molar extinction coefficient. These features suggest (see case I in

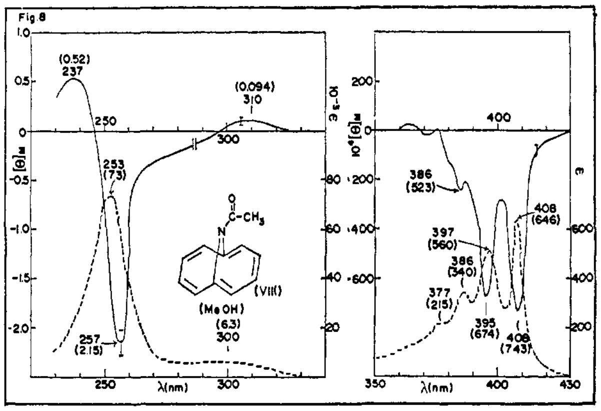

Figure 8. Absorption (- - -) and MCD (——) of N-acetyl-1,6-iminocyclodecapentaene (VIII) in MeOH.

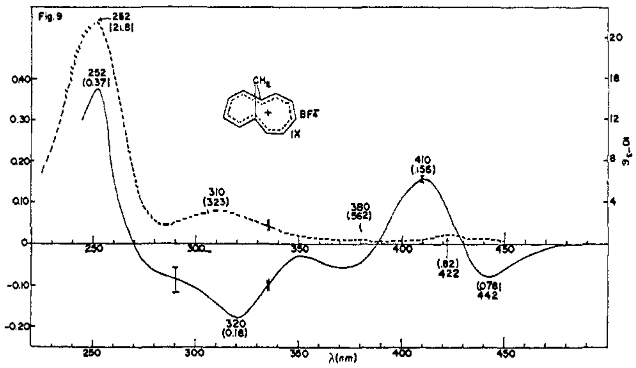

Figure 9. Absorption (- - -) and MCD (——) of 1,6-methanocycloundecapentaenyl fluoroborate (IX) in MeOH.

the previous section) a totally symmetric vibrational progression superimposed on a single quantum in this vibration.

Two other facts merit attention. First, the MCD of the 11-bromomethano derivative V (Figure 5) is very different (around 400 nm) from that of the methano compound IV discussed previously (Figure 4a). Second, considering the two dibromo derivatives VI and VII, it can be seen in Figures 6 and 7 that MCD and absorption reveal about the same sensitivity to the location of the bromines on the ring. Moreover, the MCD spectra are not fundamentally different, a result which is expected since the bromine atoms act only as a slight perturbation upon the π-electron system responsible for the absorption transitions.

D. Group 4 (Figure 9). Compound IX is also a ten-π-electron system and, as in the examples considered above, theory predicts four absorption bands. Indeed, four main bands are observed, but contrary to what is observed in the cyclodecapentaene derivatives, the two B bands (252 and 310 nm) are now widely separated. It is interesting to note that, while the two absorption components have very different intensities, the areas under the positive and negative lobes of the MCD curve seem to be of the same order of magnitude. This (near) equality of the *B* terms for two bands arising from a lifting of the degeneracy of two degenerate states is in good agreement with the theory[5] and supports the earlier statement[19] that a strong absorption band does not necessarily lead to a strong magnetic circular dichroism. Moreover, it should be emphasized that the MCD sign is negative for the absorption bands located around 310 and 380 nm while it is positive for the band at 252 nm; this result parallels that of fluorescence polarization measurements,[23] which show the first two transitions to be perpendicularly polarized to the third transition. It is also of interest to note that the absorption band located at 422 nm does not lead to a single *B* term but that at least two *B* terms of opposite sign and relatively large magnitude are observed at 410 and 442 nm.

Conclusion

In brief, the present contribution demonstrates that MCD is a suitable tool for differentiating between the various cyclodecapentaene derivatives. It was shown in particular that the general shape, sign, and magnitude of the *B* terms through the forbidden ^1L_b band is very sensitive to the nature of the substituent on the 1,6 bridge. It is thus likely that pure D_{2h} symmetry is not exactly appropriate for interpreting the MCD spectra of these compounds since deviations from planarity and perturbations of both electric and magnetic dipole moments by the 1,6 bridge seem to be of importance. On the other hand, the existence of vibrational components of different symmetry has been postulated to explain some of our MCD results for the band located at longer wavelength.

The solvent also plays an important role and may even reverse partly the sign of the *B* term, as seen, (Figure 3) for the N-methylimino derivative III in methanol and cyclohexane. This is so because the magnitude of the *B* term is proportional to the product of *three* terms which may be either *positive* or *negative*, while the absorption only depends upon the square of *one* of these terms and is therefore probably not as sensitive to the chemical perturbations. The protonation of the 1,6-imino-bridged compound I resulted in drastic changes in the MCD spectrum, a result which suggests a strong influence of the overlap integral between the nonbonding nitrogen electrons and the ten-π-electron system of the ring upon the magnetic moment between excited states.

It has been demonstrated that the sign of MCD terms depends on the relative polarization of various transitions but that the absolute polarization cannot be derived simply by a qualitative examination of the data. However, it should be emphasized that the sign of *B* terms has often been correlated, although not always unambiguously, with the known polarizations of various bands (see compounds in group 2). Thus it has been shown that *B* seems to present a different sign for electronic transitions polarized along the short or long axis of the compound under study. Also some of our results tend to support the presence of a postulated additional absorption band between ^1L_a and the ^1B pair. It is realized that detailed calculations (the interaction between L and B bands being considered) as well as additional experimental work on other systems are necessary in order to check the limits of validity of the above arguments. Although quantum mechanical data are obtainable theoretically for [10]annulene systems, it should be kept in mind that direct comparison with experiment would be difficult since the actual fre-

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(23) W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J. P. Weber, *Helv. Chim. Acta.*, 51, 225 (1968).

quency difference between the two *B* bands is hard to estimate. Finally, it is our hope that our contribution will help in shedding some light on the analytical role of *B* terms and their close relationship with other spectroscopic data.

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Reactions of Hexabromocyclopentadiene and the Synthesis of Octabromofulvalene[1]

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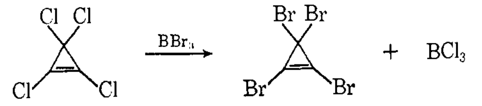
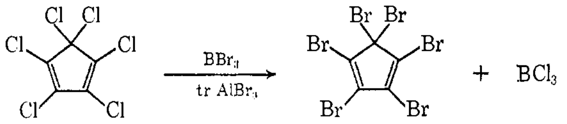
Contribution from the Chemistry Department, The University of Wisconsin, Madison, Wisconsin 53706. *Received August 21, 1967*

Abstract: Hexabromocyclopentadiene (**2**) is conveniently synthesized from hexachlorocyclopentadiene (**1**) and BBr_3 in the presence of catalytic $AlBr_3$. **2** dimerizes in the presence of larger amounts of $AlBr_3$ to form the cage compound, dodecabromopentacyclo[5.2.1.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane, $C_{10}Br_{12}$ (**3b**). Mixtures of cage compounds $C_{10}Br_nCl_{12-n}$ (**3c**) containing both bromine and chlorine were synthesized by partial halogen exchange and dimerization, starting either with **1** or **2** or mixtures of **1** and **2**. Reductive coupling of **2** with copper or CuBr gives low yields of a decabromobicyclopentadienyl, $C_{10}Br_{10}$ (**6**), which can also be obtained from the corresponding decachloro compound **4** by halogen exchange. Octabromofulvalene (**8**), a dark blue crystalline solid, is obtained from **2** by reaction with CuBr in 9:1 dimethoxyethane-water at 0°.

Recently, it was found that complete halogen exchange takes place between tetrachlorocyclopropene and boron tribromide to give, conveniently and in one step, tetrabromocyclopropene.[2] This



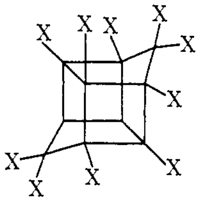
reaction is thought to occur *via* intermediate formation of aromatic trihalocyclopropenium ions.[3] For the vinylogous cyclic chlorocarbon, hexachlorocyclopentadiene (**1**), aromatic stabilization of the pentahalocyclopentadienium ions does not take place,[4] and the corresponding halogen exchange might be predicted to be more difficult. In fact, **1** is inert to boron tribromide alone, even when heated. However, a trace of aluminum tribromide serves to catalyze complete halogen exchange between **1** and BBr_3, giving hexabromocyclopentadiene (**2**). Compound **2** crystallizes



1 2

as beautiful amber-colored needles from alkanes. It has been prepared by other methods,[5] but the synthesis from **1** is quite convenient for laboratory use. This paper describes the dimerization and dehalogenation of **2**, both of which lead to products having unusual structures.

Dimerization. A famous reaction of **1** is its dimerization in the presence of aluminum chloride or other powerful Lewis acids to the "Prins dimer," dodecachloropentacyclo[5.2.1.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (**3a**).[6] With aluminum tribromide, **2** reacts in an analogous fashion at 100° to give the perbromo Prins dimer, **3b**.[7] **3b** is a colorless crystalline solid, which closely resembles **3a** in its physical properties. The melting point of **3b** is above 350°, and it is nearly insoluble in most organic solvents (recrystallization was effected from dibromomethane). The infrared spectrum of **3b** closely resembles that of **3a**. Each principal band in the spectrum of **3a** finds a counterpart at slightly longer wavelength in the spectrum of **3b**, as shown in Table I.



3a, $C_{10}Cl_{12}$ (X = Cl)
b, $C_{10}Br_{12}$ (X = Br)
c, $C_{10}Br_nCl_{12-n}$ (X = Br, Cl)

When a 1:1 mixture of **1** and **2** was treated with $AlCl_3$, a cage dimer (**3c**) containing both halogens is

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[1] Abstracted from the Ph.D. thesis of P. T. Kwitowski, University of Wisconsin, 1966.

[2] S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).

[3] R. West, A. Sadō, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).

[4] R. Breslow, R. Hill, and E. Wasserman, *ibid.*, 86, 5349 (1964).

[5] F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930).

[6] H. J. Prins, *Rec. Trav. Chim.*, **65**, 465 (1946).

[7] The use of **3b** as an X-ray opaque agent is described in a patent: C. W. Roberts and M. B. Chenoweth, U. S. Patent 3,212,973 (Oct 19, 1965). The preparation of **3b** is described in the Ph.D. thesis of R. H. Earle, Purdue University, 1957.