

# Magnetic Circular Dichroism Studies. IV.<sup>1</sup>

## Investigation of Annulene Derivatives<sup>2</sup>

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**Abstract:** Magnetic circular dichroism measurements (MCD) are reported for 12 conjugated hydrocarbons through their visible and near-ultraviolet (down to 230 nm) absorption bands. Special emphasis has been put on [18]annulene as well as many of its derivatives where either one or two double bonds have been replaced by acetylene linkages or the six inner hydrogens have been substituted by bridges (oxygen, sulfur, and combinations of these). These MCD measurements provide additional evidence for the utility of this technique as an analytical tool. Moreover, most of our results can be qualitatively understood in terms of recent theoretical developments. A simple model is described for the mathematical analysis of MCD curves and the quantitative derivation of the molecular parameters of interest. The method is used to obtain experimentally the magnetic moment of degenerate excited states in molecules possessing at least a threefold symmetry axis. An attempt is also made to discuss MCD spectra of molecules of lower symmetry and some unresolved problems are underlined.

Interest in Faraday effect (or magneto-optical activity) measurements through absorption bands has been revived in recent years with the availability of very sensitive photoelectric spectropolarimeters. New theoretical developments followed<sup>4</sup> which in turn stimulated intense work in a number of laboratories. Theoretical interest has moved naturally toward the study of symmetrical inorganic,<sup>5-7</sup> biological,<sup>8,9</sup> and organic compounds,<sup>10,11</sup> where a direct comparison between experimental and quantum mechanically predicted parameters is usually possible. It has been shown that the technique provides a new and powerful means of determining the nature of the excited states of ions<sup>5</sup> and molecules<sup>10</sup> and allows their magnetic moment (if present) to be determined experimentally. It should be kept in mind, however, that inorganic and organic chemists are also interested in the potential application of the Faraday effect as an analytical tool, especially in structural problems. Therefore, a wide range of samples has to be scrutinized in order for correlations to be made. Such work is now in progress in our laboratory, similar to our earlier approach<sup>12</sup> in developing optical rotatory dispersion as a tool in organic chemistry.

The theoretical and analytical aspects of magneto-optical activity have already been emphasized in a previous paper<sup>1</sup> and the same approach will be followed in the present contribution. It should be recalled that the phenomenon may be investigated either by magneto-optical rotatory dispersion (MORD) or by magnetic circular dichroism (MCD) and that both provide the same kind of information. For reasons which have already been discussed,<sup>5,13</sup> emphasis has been put on the latter in our laboratory.

We deal here with MCD studies of a large number of annulenes and dehydroannulenes containing 8, 14, 16, and 18 carbon atoms in the ring. Most of these compounds were first synthesized and studied by Sondheimer's group and they have been the subject of a recent review paper.<sup>14</sup> Dehydroannulenes are derivatives in which one or more of the double bonds have been replaced by acetylene linkages. Special emphasis has been given here to [18]annulene as well as to some of its heterocyclic analogs in which the six inner hydrogen atoms have been replaced by bridges (oxygen, sulfur, and combinations of these). In addition, the MCD spectra of dimethyldihdropyrene as well as a few absorption measurements at liquid nitrogen temperature ([18]annulene disulfide oxide and [18]annulene trisulfide; 1,8-bisdehydro[14]annulene) have been included for convenience.

These compounds offer additional evidence for the utility of MCD as an analytical tool. Moreover, they include molecules of high symmetry ( $D^{6h}$  in [18]annulene) as well as molecules of lower symmetry (without a threefold axis of symmetry), many of them having strongly delocalized  $\pi$  electrons and thus possessing aromatic character. It is pertinent to note that [18]annulene has basically the same  $18\pi$ -electron framework as that of the previously reported<sup>1</sup> chlorins. It is hoped, therefore, that both series may be subjected to a common theoretical treatment<sup>15</sup> (for example, on the

(1) Paper III: B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 6170 (1967).

(2) We are indebted to the National Science Foundation (Grant No. GP-4304) and to the National Institutes of Health (Grant No. GM-12173) for financial aid.

(3) (a) 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 5<sup>e</sup>; (b) NSF predoctoral fellow.

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(10) P. J. Stephens, P. N. Schatz, A. B. Ritchie, and A. J. McCafferty, *J. Chem. Phys.*, in press.

(11) J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **89**, 30 (1967).

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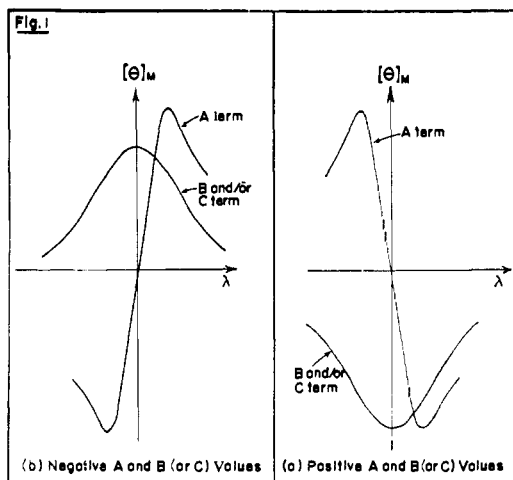


Figure 1. Characteristic shapes of MCD dispersion curves.

basis of the free electron model<sup>16</sup>), which might lead to a quantitative prediction of the experimentally determined molecular parameters.

### Experimental Section

The instrumentation involved in our MCD measurements has already been discussed.<sup>1</sup> Throughout the course of this work, the experiments were conducted with the use of a 50-kgauss magnetic field generated by a Lockheed superconducting magnet (Model OSCM-103). As in the case of natural optical activity,<sup>17</sup> the variable used to measure magnetic circular dichroism may be chosen to be either circular dichroic absorption,  $\Delta\epsilon$ , or molar ellipticity,  $[\theta]_M$ . The use of  $\Delta\epsilon$  is particularly easy to justify on a physical basis, but  $[\theta]_M$  is more convenient for comparison of MCD and MORD results. Both are then expressed in terms of the same unit and the experimentally observed extrema have comparable magnitudes.<sup>4,5</sup> Use has been made of the molar ellipticity ( $[\theta]_M$  in deg gauss<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) in this laboratory, with the sign convention previously adopted.<sup>1,5</sup>

The samples investigated are listed in Table I together with the

Table I. List of Compounds

Name	Figure
1,7,13-Tridehydro[18]annulene (I)	2
[18]Annulene (II)	3
[18]Annulene trioxide (III)	4
[18]Annulene dioxide sulfide (IV)	5
[18]Annulene disulfide oxide (V)	6a
[18]Annulene trisulfide (VI)	6b
Monodehydro[14]annulene (VII)	7
1,8-Bisdehydro[14]annulene (VIII)	8
<i>trans</i> -15,16-Dimethyldihydropyrene (IX)	9
1,9-Bisdehydro[16]annulene (X)	10
[16]Annulene (XI)	11a
[8]Annulene or cyclooctatetraene (XII)	11b

number of the corresponding figure which includes the structural formula, the absorption spectrum, and the MCD curve. Samples III-VI were kindly provided by Badger;<sup>18</sup> they are stable and were therefore used without further purification. Their absorption spectra (in ethanol) proved to be in good agreement with the literature values<sup>18</sup> except for the dioxide sulfide (IV) in which  $\epsilon$  at 342 nm was found to be 190,000, as compared to 95,000 (apparently due to a printing error in view of the good agreement for the other

absorption bands). The [18]annulene, as well as the dehydro derivatives, were generously supplied by Sondheimer,<sup>14</sup> whereas [16]annulene was a gift of Professor G. Schröder. The relative instability of these molecules made their purification necessary just before use. These samples were obtained in solution and the solvent was removed at room temperature under vacuum. The residue was then taken up in ether (or chloroform) and the solution passed through a short column of neutral alumina (Merck, activity 1). The solvent was removed under reduced pressure and the residue dissolved in spectrograde isooctane for MCD and absorption measurements. The molar concentrations of these solutions were determined from  $\epsilon_{\max}$  values published in the literature.<sup>14</sup> Cyclooctatetraene was of commercial origin and was purified by vpc. Dimethyldihydropyrene was kindly provided by Boekelheide<sup>19</sup> and was used without further purification. It should be pointed out, however, that the solution of this compound in cyclohexane is rather unstable and the intensity of the absorption bands decreases as a function of time. Our freshly prepared solution had  $\epsilon_{\max}$  values about 30% lower than those found in the literature.<sup>19</sup> This should not be too critical as the same solution was used in our MCD work and therefore the same error affects both  $\epsilon$  and  $[\theta]_M$  to the same extent.

### Results

Before going through a detailed examination of our results, we want to draw attention to a major difference between circular dichroism (CD, only observed for optically active molecules) and magnetic circular dichroism (MCD, observed for either optically active or inactive materials). In CD, dispersion curves for a single absorption line have a typical bell shape. On the other hand, MCD dispersion curves show two kinds of terms which have a different wavelength dependence: the *A* term is S shaped (similar to the Cotton effect observed in natural optical rotatory dispersion), whereas the *B* (or *C*) term has a bell shape (no equivalence in natural rotation but similarity in natural circular dichroism). Despite these superficially similar common features between CD and MCD, it should be kept in mind that *the two techniques can by no means lead to the same kind of information.*

It follows from the above arguments that the magnetic molar ellipticity,  $[\theta]_M$ , is most of the time a combination of *A* and *B* (or *C*) terms.<sup>4</sup> Their wavelength dependence is shown in Figure 1 for either positive (a) or negative (b) *A, B, or C values.*<sup>1</sup> We shall now discuss our MCD results (Figures 2-11) in relation to the absorption spectra and point out those features which are of analytical value.

**Samples I-IV (Figures 2-5).** The general characteristics of the absorption spectra of these molecules are the same: a very strong band (band I) occurs between 330 and 370 nm ( $\epsilon$  302,000 at 368 nm in Figure 3), a band of moderate intensity (band II) lies in the range 400-450 nm ( $\epsilon$  22,100 at 448 nm in Figure 3), and a large number of additional shoulders have been noted through the whole spectral range. However, the location and intensity of the bands varies from one molecule to another. As an example, in passing from [18]annulene (II) to the tridehydro[18]annulene (I), band I shifts from 368 to 335 nm and its intensity is lowered from 302,000 to 170,000. Samples I and IV were also examined above 450 nm where the molar extinction coefficient  $\epsilon$  is low ( $\epsilon < 100$  for I). Unfortunately, owing to the scarcity of samples II and III, a sufficiently concentrated solution could not be obtained in order to run their spectra in the same range.

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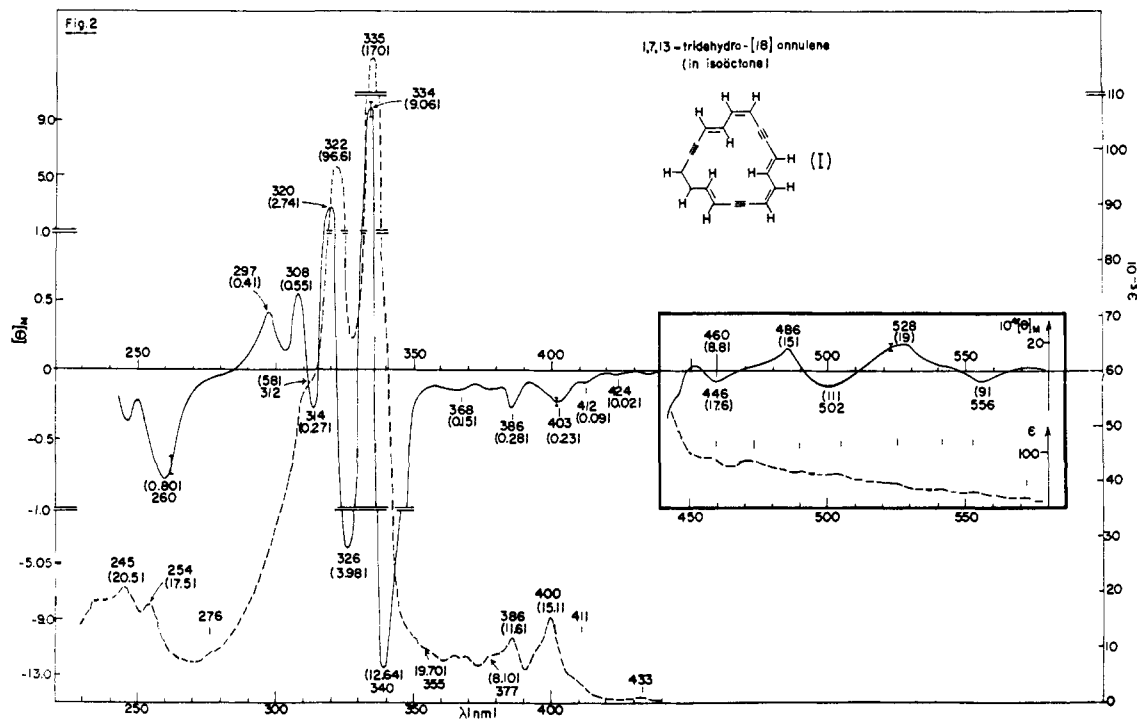


Figure 2. Absorption (---) and MCD (—) of 1,7,13-tridehydro[18]annulene (I).

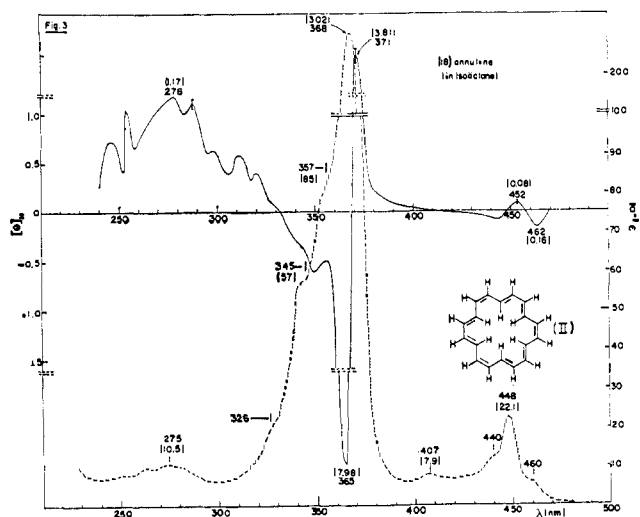


Figure 3. Absorption (---) and MCD (—) of [18]annulene (II).

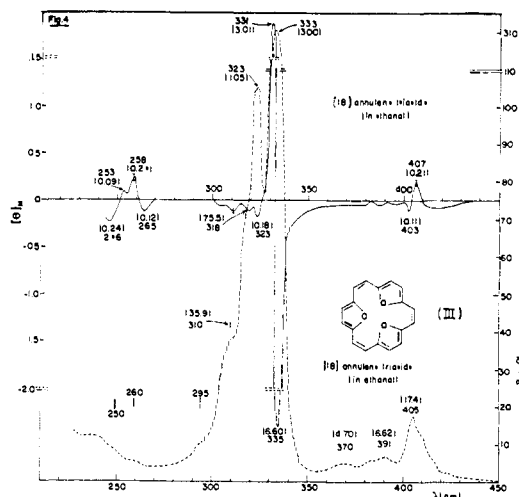


Figure 4. Absorption (---) and MCD (—) of [18]annulene trioxide (III).

Figures 2–5 also exhibit the same basic features in terms of their MCD spectra. A well-defined S-shaped curve (characteristic of an *A* term) occurs through band I, the wavelength corresponding to the inflection point being coincident with that of the absorption maximum within the experimental error (exactly in Figures 2 and 3 and within a 2-nm range in Figures 4 and 5). However it is interesting that the *A* value is of a *different sign* for [18]annulene and for samples I, III, and IV (see Figure 12). It should also be pointed out that there is *no simple relationship* between the peak-to-peak MCD value (see column 8 in Table II) and the corresponding maximum molar extinction coefficient  $\epsilon_m$ . For instance,  $\epsilon_m$  is about the same for [18]annulene (II) and the trioxide derivative (III) but the difference values range from +11.79 for the former to -9.61 for the latter.

The MCD spectra corresponding to band II shows a more complicated structure. No evidence is found, however, of a typically S-shaped curve. It seems more likely to assume *B* terms corresponding to the various vibrational components, especially since the MCD extrema occur at wavelengths almost coincident with those of absorption maxima. Inspection of the 450–600-nm region in Figures 2 and 5 leads to the conclusion that the MCD spectra are much better resolved than the absorption spectra when both are run at the same concentration. Another spectral feature worth noting concerns the blue side of band I. Whereas  $\epsilon_{\max}$  ranges between 10,000 and 20,000 below 300 nm, the relative variations in  $[\theta]_M$  are much greater (from 1.17 in Figure 3 to 0.24 in Figure 4) and  $[\theta]_M$  may be either positive (at 278 nm in Figure 3) or negative (at 260 and 293 nm in Figures 2 and 5, respectively).

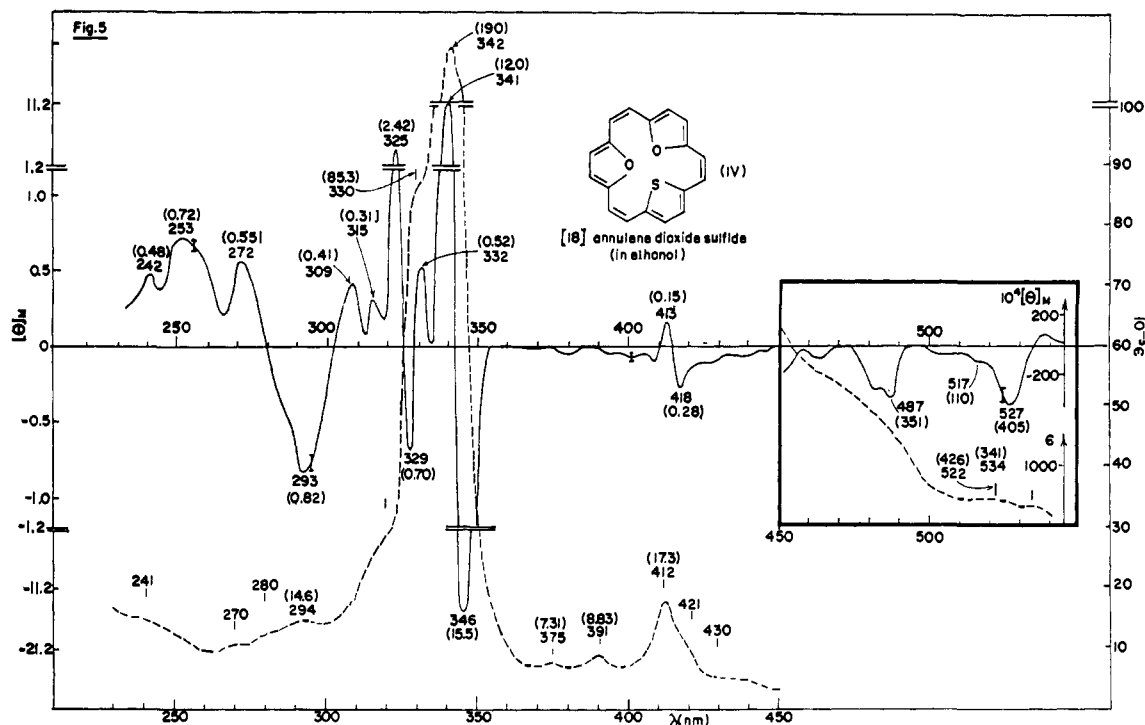


Figure 5. Absorption (---) and MCD (—) of [18]annulene dioxide sulfide (IV).

**Samples V and VI (Figure 6).** Bands I and II are also discernible in the disulfide oxide (Figure 6a) and trisulfide (Figure 6b), although the spectra are con-

6a) seem to be consistent with *B* dispersion terms, since the  $[\theta]_M$  occur at wavelengths not too far removed from those of the absorption maxima. Two MCD peaks

**Table II.** Experimental Determination of the Magnetic Moment between a Pair of Degenerate Excited States

Compound	$\lambda_0$ , nm ( $\nu_0$ , $\text{cm}^{-1}$ )	$\Gamma$	$A/D$	$\mu$	$[\theta_1]_M$	$[\theta_2]_M$	(Dif)	<i>S</i>	$B/D$ $\times 10^5$	$\epsilon_{\text{max}}$
[18]Annulene	368	800	-0.061	+0.122	+3.81	-7.98	+11.79	-4.17	+4.80	302,000
[18]Annulene trioxide	333 30,000	600	+0.038	-0.076	-6.60	+3.01	-9.61	-3.59	+4.16	300,000
[18]Annulene dioxide sulfide	342 29,300	1000	+0.285	-0.57	-15.50	+12.00	-27.50	-3.50	+6.40	190,000
Tridehydro- [18]annulene	335 29,800	800	+0.201	-0.40	-12.64	+9.06	-21.70	-3.58	+9.10	170,000

siderably simplified. In the former, we observe two broad bands partially resolved into a number of components, whereas this resolution does not occur in the latter. Of interest is the fact that the intensity of the two main bands is considerably lowered when going from [18]annulene (II) to the trisulfide VI, *i.e.*, when reducing the symmetry of the framework through overcrowding of inner atoms and subsequent twisting of the molecule. As an example,  $\epsilon_m$  for band I is 302,000 for [18]annulene (II) but only 28,000 and 17,000 for the disulfide oxide V and trisulfide VI, respectively. It should be noted that the lowering of the allowed nature of this transition is accompanied by a loss of aromaticity for the molecule.<sup>14</sup> Absorption measurements at liquid nitrogen temperature (Figure 13a and b) lead to a better resolution of the spectra: the visible part of the spectrum of the trisulfide shows at least three components (at 380, 402, and 422 nm) as in the case of the disulfide oxide; however, band I in the trisulfide remains still unresolved.

The features of the MCD spectra for the bands at longer wavelengths (385, 400, and 422 nm in Figure

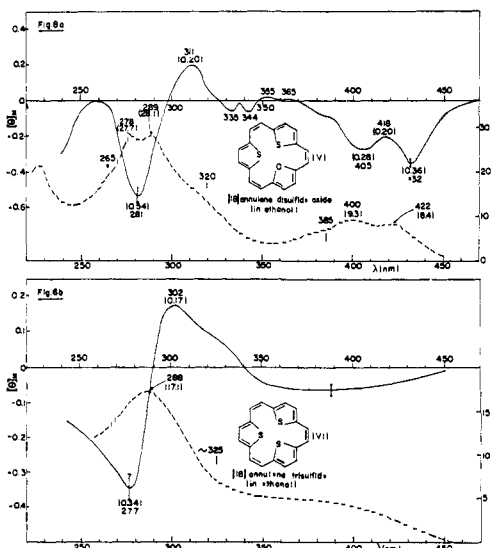


Figure 6. Absorption (---) and MCD (—) of (a) [18]annulene disulfide oxide (V); (b) [18]annulene trisulfide (VI).

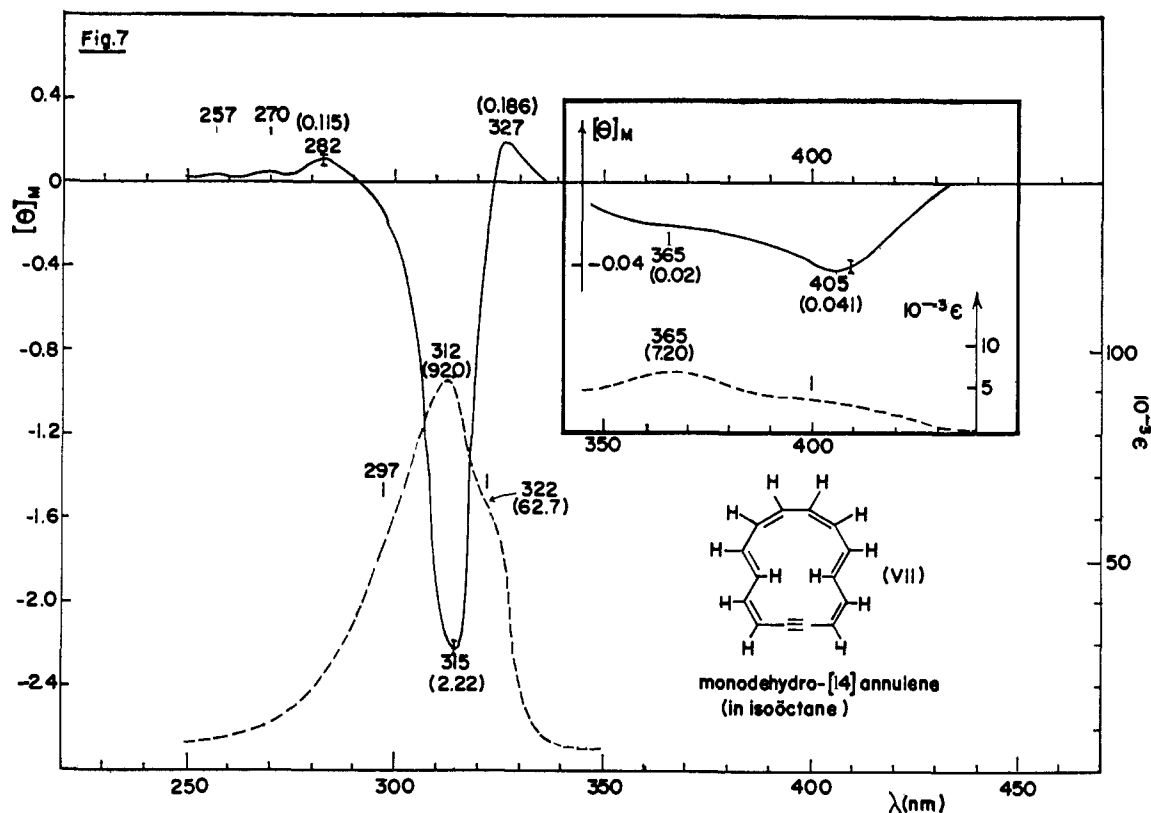


Figure 7. Absorption (---) and MCD (—) of monodehydro[14]annulene (VII).

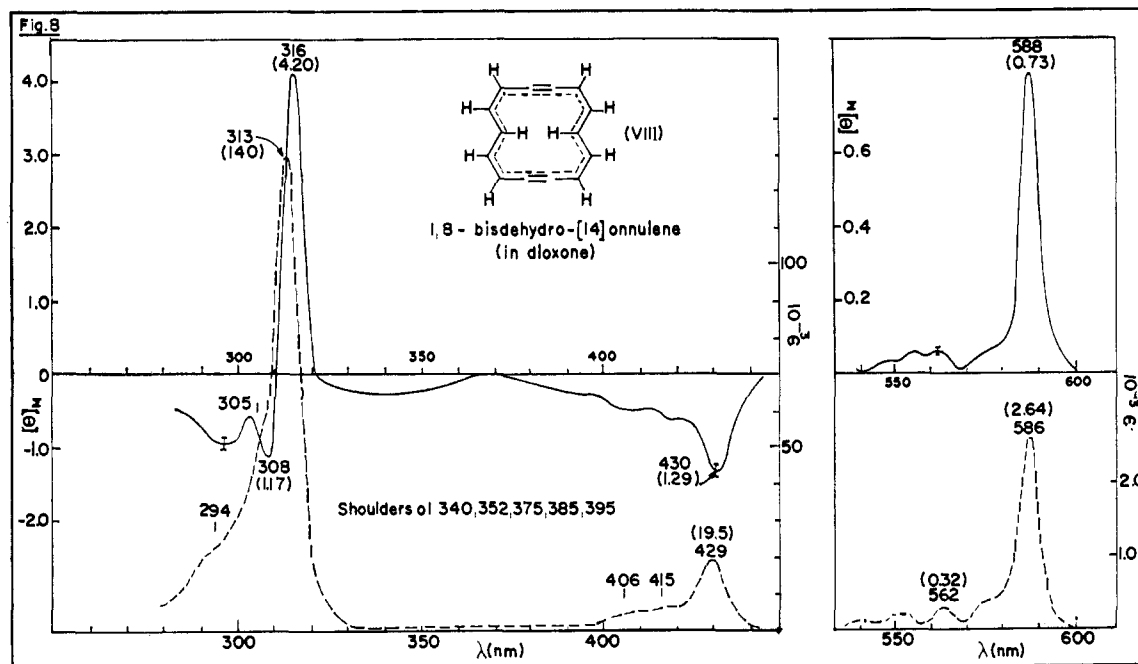


Figure 8. Absorption (---) and MCD (—) of 1,8-bisdehydro[14]annulene (VIII).

occur at 335 and 344 nm, respectively, in Figure 6a, which have no obvious counterpart in the absorption spectrum. An S-shaped MCD curve is observed through band I in the trisulfide (Figure 6b) but the situation in the same spectral region of the disulfide oxide (Figure 6a) is very ambiguous. At the present time, it seems to us unreasonable to make any attempt in assigning these features in Figure 6a to either *A* or *B* dispersion terms. MCD measurements at low tem-

peratures are likely to be of some help in solving this problem in the future.<sup>1</sup>

**Sample VII (Figure 7).** The MCD spectrum shown in Figure 7 seems consistent with a number of *B* dispersion terms. This is supported by the fact that extrema occur at wavelengths very close to those of the corresponding absorption maxima. The  $[\theta]_M$  maximum values are either positive (at 327 or 282 nm) or negative (315, 365, and 405 nm). It is also of interest

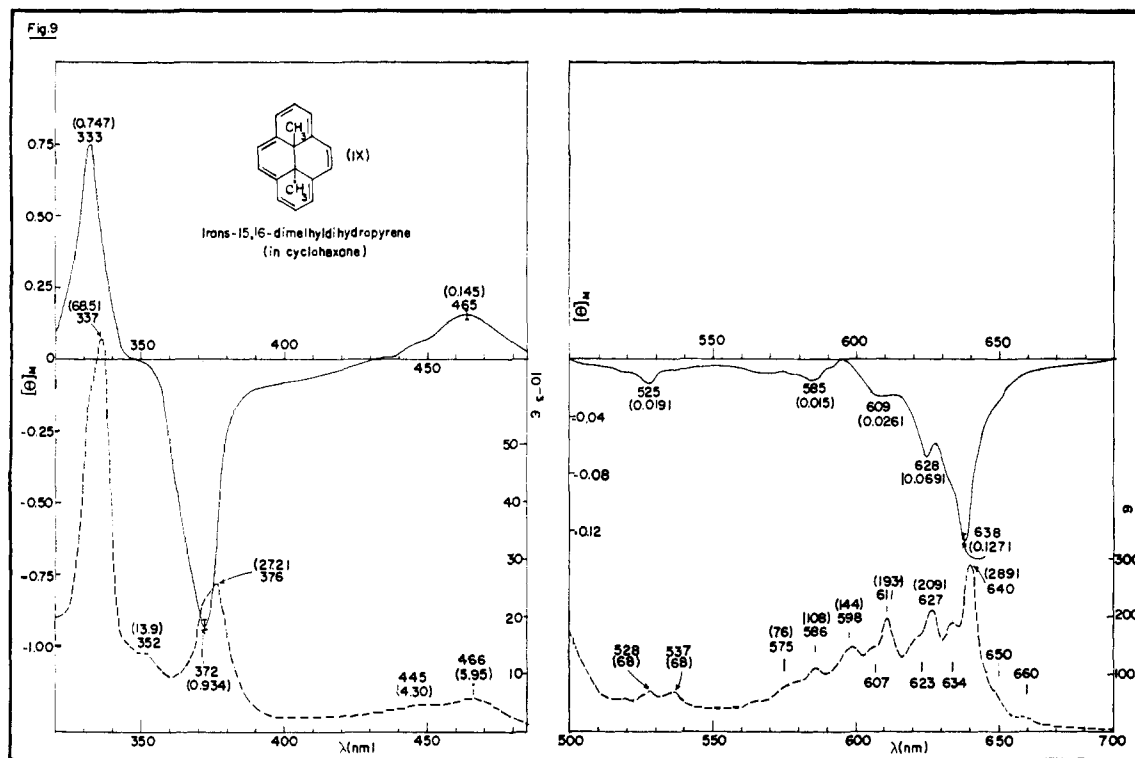


Figure 9. Absorption (---) and MCD (—) of *trans*-15,16-dimethyldihydropyrene (IX).

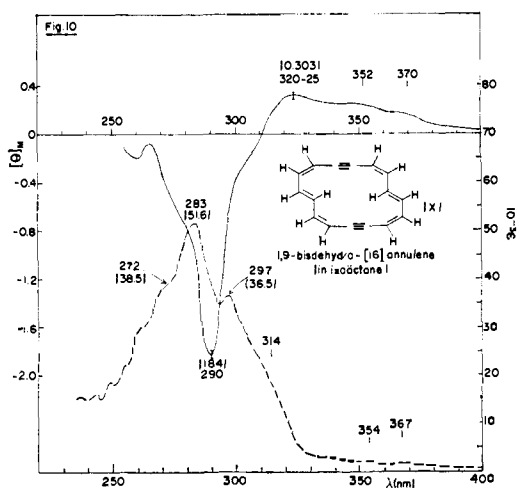


Figure 10. Absorption (---) and MCD (—) of 1,9-bisdehydro[16]annulene (X).

to note that, whereas the absorption band around 400 nm is weaker than the one at 365 nm, the situation is reversed in the MCD spectrum. Moreover, the shoulders which occur below 300 nm on the MCD curve have no resolved counterparts in the absorption spectrum.

**Sample VIII (Figure 8).** The absorption of this 14  $\pi$ -electron system shows three groups of bands centered at 586, 429, and 313 nm, the latter being resolved into a large number of components at liquid nitrogen temperature (see Figure 13c). The MCD dispersion terms are of type B for the two bands located at longer wavelengths. It should be noted, however, that B values are of opposite signs for the two bands and that the ratio of the maximum molar ellipticity to the maximum molar extinction coefficient is much larger at 586 nm

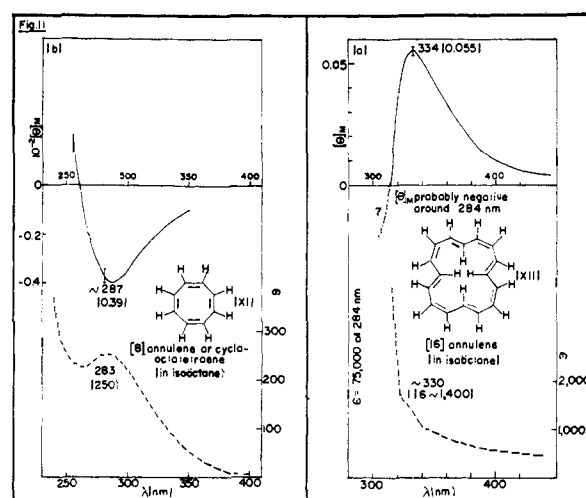


Figure 11. Absorption (---) and MCD (—) of (a) [16]annulene (XII); (b) [8]annulene (XI).

than at 429 nm ( $28 \times 10^{-5}$  and  $6 \times 10^{-5}$ , respectively). On the other hand, the shape of the MCD curve through the strongest band may be understood by assuming contributions of both A and B type (negative A value) or more likely by considering only B terms of opposite signs (the excited states being "nearly" degenerate). Once again, MCD measurements at low temperature would probably throw some light on this question.

**Sample IX (Figure 9).** This 14 $\pi$ -electron molecule differs from the previous one in that there are two methyl groups intruding into the cavity of the electron cloud.<sup>19</sup> Four main bands occur in the absorption spectrum and only B terms are found in the MCD curve. A number of interesting features merit stressing. First,  $\epsilon$  is about ten times smaller than in VIII for the

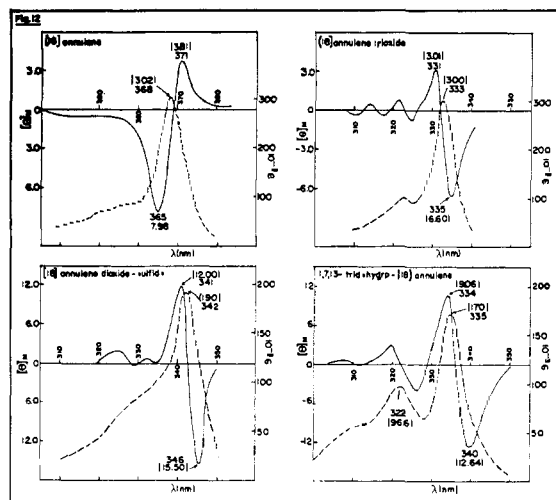


Figure 12. Absorption (---) and MCD (—) of molecules I, II, III, and IV (expanded abscissa scale and reduced ordinate scale).

band located in the near-infrared region ( $\epsilon$  289 as compared to 2640). Second, the maximum  $[\theta]_M$  values corresponding to the various bands seem to be of opposite sign when one considers the two molecules (compare  $+0.145$  at 465 nm in Figure 9 to  $-1.29$  at 430 nm in Figure 8). Third, instead of having a possible  $A$  term at lower wavelengths (as in VIII), we now observe two  $B$  terms of opposite sign. This situation can tentatively be understood in terms of a lifting of the possible near-degeneracy in IX of the corresponding excited state (in bisdehydro[14]annulene), owing to the steric and electronic interaction of the  $\pi$  electrons of IX with the methyl groups.

**Samples X, XI, and XII (Figures 10 and 11).** The absorption spectra of 1,9-bisdehydro[16]annulene (X) and [16]annulene (XII) show somewhat similar features (maximum at 283 and 284 nm with  $\epsilon$  51,600 and 75,000, respectively), although that of X is much better resolved, even at room temperature. [16]Annulene is a rather unstable molecule; we were unable to measure the MCD spectrum below 310 nm with a sufficient degree of certainty but a minimum ( $[\theta]_M$  of the order of  $-1$ ) seems to occur around 284 nm. However, there is definitely a positive maximum at 334 nm (see Figure 11a) corresponding to a slight shoulder on the corresponding absorption spectrum. In the case of [8]annulene (cyclooctatetraene), a negative  $[\theta]_M$  value was encountered in the region of the absorption maximum (at 283 nm in Figure 11b), but MCD measurements could not be performed through the strong band around 220 nm.

In concluding this section, two points should be emphasized. (1) The main interest of MCD as an analytical tool lies in the fact that a given absorption band may correspond to either an  $A$  or a  $B$  term (or both) and that their value may be either positive or negative. As pointed out earlier,<sup>20,21</sup> this latter fact may be understood physically in a simple way: whereas the maximum absorption is proportional to the square of a matrix element (and therefore positive), matrix elements with their sign enter into the quantum mechan-

(20) I. Tinoco, Jr., and C. A. Bush, *Biopolymers Symp.*, 1, 235 (1964).

(21) B. Briat, Ph.D. Thesis, University of Paris, 1966.

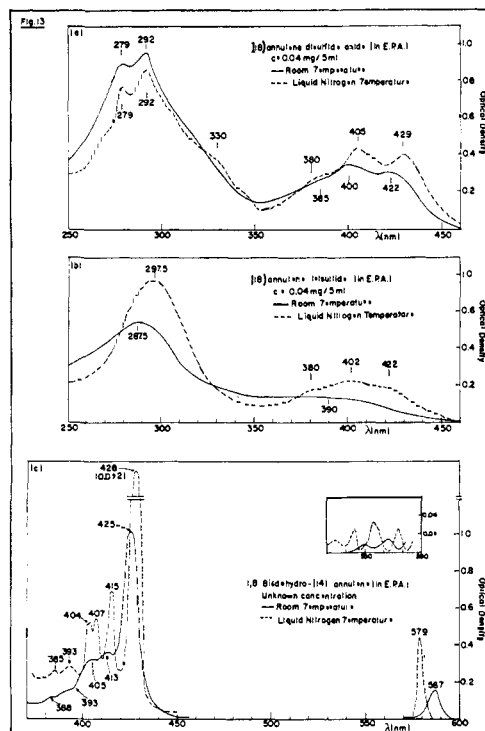


Figure 13. Absorption spectra at room (—) and liquid nitrogen temperature (---) of (a) [18]annulene disulfide oxide; (b) [18]annulene trioxide, and (c) 1,8-bisdehydro[14]annulene.

ical expression for  $A$  and  $B$ . (2) A strong absorption band does not lead necessarily to a large magnetic circular dichroism; this has been illustrated in a number of examples and additional evidence will be given in the near future.

## Discussion

This section is devoted to the spectroscopic aspect of the problem and is divided into four parts. First, we summarize some qualitative theoretical predictions. We then report a simple way of determining parameters of theoretical interest from the experimental curves (mathematical analysis). The assignment of the absorption bands of the more symmetrical annulenes follows in the third part, which finally allows a qualitative comparison to be made between theory and experiment. It may be pointed out, however, that we restricted ourselves to the major features of a limited number of spectra (the more symmetric compounds).

**1. Qualitative Theoretical Predictions.** Considering a single absorption line, the molar ellipticity  $[\theta]_M$  (in  $\text{deg gauss}^{-1} \text{cm}^2 \text{mole}^{-1}$ ) may be expressed<sup>1,4</sup> as  $[\theta]_M = -21.348 \{f_1 A + f_2 [B + (c/kT)]\}$ , where  $f_1$  and  $f_2$  are functions of the frequency  $\nu$  of the incident light. Assuming a damped oscillator model for the shape of the absorption band, one has

$$f_1 = \frac{\nu^3 \Gamma}{[\nu_0^2 - \nu^2]^2 + \nu^2 \Gamma^2}; \quad f_2 = \frac{4\nu_0 \nu^3 [\nu_0^2 - \nu^2] \Gamma}{h[(\nu_0^2 - \nu^2)^2 + \nu^2 \Gamma^2]}$$

where  $\nu_0$  stands for the frequency of maximum absorption and  $\Gamma$  for the width at half-maximum absorption;  $\nu_0$ ,  $\nu$ , and  $\Gamma$  are expressed in  $\text{cm}^{-1}$  and  $h$  is the Planck constant. Use has also been made of a gaussian function<sup>6,7</sup> to fit the absorption curve. The technique employed by Margerie<sup>22</sup> is very similar; however,

(22) J. Margerie, *Physica*, 33, 238 (1967).

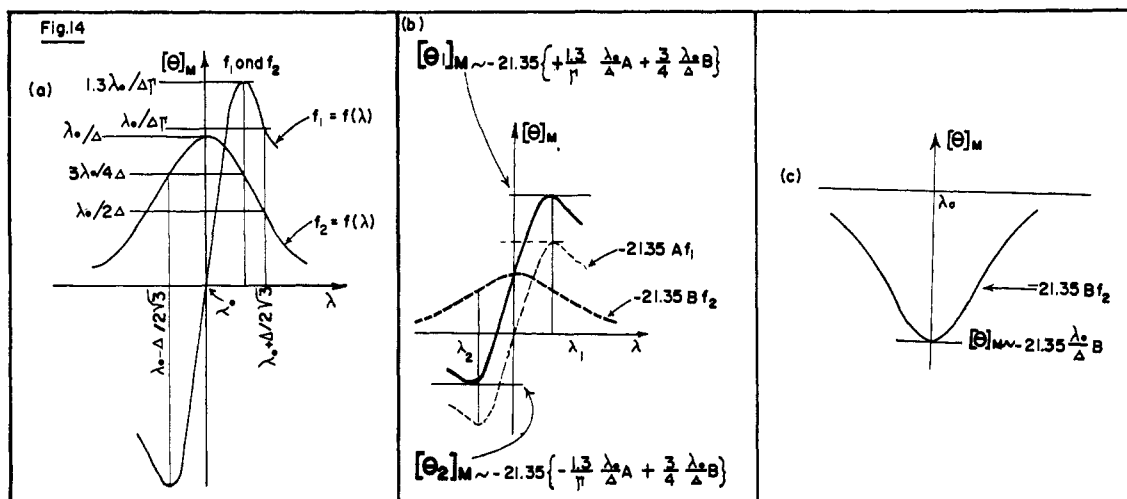


Figure 14. Mathematical analysis of an experimental curve (a) wavelength dependence of functions  $f_1$  and  $f_2$ ; (b) an  $A$ - and a  $B$ - (and/or  $C$ -) type dispersion terms are present in the curve; (c) only the  $B$  (and/or  $C$ ) term is present.

instead of choosing *mathematical* expressions for  $f_1$  and  $f_2$ , he assumes that the curve  $[\theta]_M = f(\lambda)$  is a linear combination of the *actual* absorption curve and of its first derivative. All methods have their own merit and it should be recognized that in most cases the computed values of the  $A$ ,  $B$  (and/or  $C$ ) parameters do not depend too much upon the assumed shape of the absorption band.<sup>4</sup> It is of interest to note here that the  $B$  and  $C$  dispersion terms have the same wavelength dependence. As already stated,<sup>1,4</sup> they can be separated by low-temperature measurements only ( $B$  being temperature independent, whereas the  $C$  term is inversely proportional to the absolute temperature  $T$ ). The wavelength dependence of the functions  $f_1$  and  $f_2$  is shown in Figure 14a, together with their value for a number of characteristic wavelengths.

MCD measurements thus provide  $A$ ,  $B$  (and/or  $C$ ) values which, in turn, lead to information about the electronic states of the molecule and about the molecular orbitals used to describe them. Their quantum mechanical expression has been given elsewhere<sup>4,5,8</sup> but, from a qualitative point of view, it is only necessary to understand their physical meaning: a  $C$  term arises when the ground state is degenerate; an  $A$  term is observed when either the ground or the excited state of the compound is degenerate; a  $B$  term originates from a mixing of the wave functions of the ground and excited states with some other states. Actually, the parameters of theoretical interest have been shown to be  $A/D$  and  $[B + (C/kT)]/D$ , where  $D$  is the oscillator strength of the particular spectral line.

**2. Extraction of Parameters from the Data.** Focusing now our attention on the damped oscillator model alone, we use a technique outlined elsewhere<sup>21</sup> to show how these parameters can be derived simply by considering the extrema of the recorded MCD curve. Two extreme cases will be considered in order to make the procedure clear. We first assume that the experimentally observed MCD curve is  $S$  shaped (see Figure 14b). This happens when the  $A/B$  ratio is greater than or at least equal to  $0.5\Gamma$ .<sup>23</sup> If  $[\theta_1]_M$  and  $[\theta_2]_M$  are the maximum values (*with their sign*) of the molar

(23) This 0.5 numerical coefficient has only significance as an order of magnitude.

ellipticity for the peaks at longer wavelength ( $\lambda_1$ ) and shorter wavelength ( $\lambda_2$ ) and  $S$  and (Dif) stand for their sum and difference, respectively, it follows from Figure 14b that

$$A \sim -\frac{1}{55.4} \frac{\Delta}{\lambda_0} (\text{Dif})/\epsilon_m \quad (1)$$

$$B + (C/kT) \sim -\frac{1}{32} \frac{\Delta}{\lambda_0} S \quad (2)$$

where  $\Delta$  (band width) and  $\lambda$  (wavelength of maximum absorption) are expressed in the same units (here nanometers) and  $\Gamma$  is expressed in  $\text{cm}^{-1}$ . These expressions lead to the proper sign for  $A$  and  $B$  (and/or  $C$ ) values.

The dipole strength of the relevant transition may then be estimated from  $D \sim 9.2 \times 10^{-3} \epsilon_m \Delta/\lambda_0$  where  $\epsilon_m$  is the maximum molar extinction coefficient. It becomes clear that  $A/D$  and  $[B + (C/kT)]/D$  can be expressed simply by

$$A/D \sim -1.97\Gamma(\text{Dif})/\epsilon_m \quad (3)$$

$$[B + (C/kT)]/D \sim -3.47(S/\epsilon_m) \quad (4)$$

A number of interesting properties follow from this derivation. First the difference (Dif) or the sum ( $S$ ) as well as  $\epsilon_m$  are here expressed as molar values but the same result would be obtained in considering the measured ellipticity (standardized to 1 gauss) and optical density of the same sample under the same length. Second, the term (Dif) is the peak-to-peak magnitude of the  $S$ -shaped term and is known with good accuracy. On the other hand, an incorrect position of the base line may have dramatic consequences in the determination of  $S$  and, consequently, of  $B$  (or  $C$ ). Finally  $A/D$  and  $B/D$  (in the particular case where  $C$  is zero) are molecular parameters which should be independent of the temperature  $T$  (when one considers a single absorption line);  $S$  should therefore be also independent of  $T$  whereas (Dif) should increase when  $T$  decreases, owing to the dependence of the band width on the absolute temperature.

Alternatively, let us assume that the  $A$  value is predicted to be zero or that, at least, the  $A$  dispersion term cannot be recognized clearly on the experimental curve.



Table III. Extraction of Useful Parameters from Published Experimental Data

Sample	$\lambda_0$ , nm	$\Gamma$ , cm <sup>-1</sup>	Present analysis <sup>c</sup>		Values found in the literature <sup>d</sup>	
			$A/D$	$[B + (C/kT)]/D$	$A/D$	$[B + (C/kT)]/D$
Coronene <sup>a</sup>	304	~400 <sup>e</sup>	+0.18		+0.18	
K <sub>2</sub> CrO <sub>4</sub> <sup>a</sup>	373	4085	-0.49	+1.6 × 10 <sup>-6</sup>	-0.53	+1.6 × 10 <sup>-5</sup>
K <sub>3</sub> FeCN <sub>6</sub> <sup>b</sup>	418	5572		-5.20 × 10 <sup>-3</sup>		-4.60 × 10 <sup>-3</sup>
	300	2916		+3.10 × 10 <sup>-3</sup>		+3.40 × 10 <sup>-3</sup>

<sup>a</sup>  $A$  and  $[B + (C/kT)]$  both present (use of eq 3 and 4). <sup>b</sup>  $A$  is assumed to be negligible and eq 5 is used. <sup>c</sup> Experimental data are taken from ref 10 (coronene) and 5. However, the same  $A/D$  ratio was also obtained from our own unpublished measurements of coronene. <sup>d</sup> See ref 10 (coronene) and 5 for the computed best fit. <sup>e</sup> As estimated from the absorption spectrum measured in our laboratory.

A bell-shaped curve is then observed (Figure 14c) and one obtains

$$[B + (C/kT)]/D \sim -5.12[\theta]_{M_{\max}}/\epsilon_m \quad (5)$$

where  $[\theta]_{M_{\max}}$  stands here for the maximum value of the molar ellipticity, this maximum occurring at a wavelength very close to or coincident with that of the absorption maximum.

The first situation ( $A/B > 0.5$ ) is oversimplified in that the extrema of the experimental MCD curve are assumed to occur at the same wavelengths as those of a pure  $A$ -type dispersion term. It should be pointed out, however, that our model still holds approximately valid in intermediate situations, *i.e.*, when both  $A$  and  $B$  (or  $C$ ) are detectable on the recorded curve. A good example is provided in eq 4 and 5. When either  $[\theta_1]_M$  or  $[\theta_2]_M$  tends to be zero,  $S$  tends to be  $[\theta]_{M_{\max}}$  and therefore the  $[B + (C/kT)]/D$  ratios as calculated from eq 4 and 5 lead to a difference of 50% (maximum possible error). In practice, as it is usually easy to choose reasonably between the two ( $S$  and bell) models, the error is below the 50% limit. Moreover, it must be kept in mind that, considering the present stage of the theory of the Faraday effect,<sup>4</sup> even a rough estimate of  $A/D$  and  $[B + C/kT]/D$  is of very great value.

Some comparisons can now be made of the results obtained by the present technique and those recorded in the literature through the use of a more sophisticated procedure<sup>5,10</sup> (computed best fit). The agreement between the two sets of values is quite good (see Table III) and thus affords some confidence in the utility of the present technique.

**3. Assignment of Absorption Bands.** Since the pioneer work of Longuet-Higgins and Salem,<sup>24</sup> many attempts have been made to explain quantitatively the absorption spectrum of [18]annulene.<sup>25</sup> All molecular orbital treatments based on the assumption of no bond alternation failed in that they led to excessively low energies and excessively large oscillator strengths. On the other hand, the hypothesis of bond alternation was not supported by X-ray diffraction measurements.<sup>26</sup> The situation has been recently reviewed by Salem<sup>27</sup> and a possible explanation provided for the discrepancy between the previously invoked schemes. A molecular distortion is assumed, owing to a slight overcrowding of the internal hydrogens. This tends to lengthen the

outer C-C bonds with respect to the inner ones, a result which is in agreement with published data.<sup>28</sup> According to this explanation, C<sub>18</sub>H<sub>18</sub> should keep its center of symmetry and consequently its D<sub>6h</sub> symmetry. From a qualitative point of view, the symmetry (and eventually degeneracy) of the ground and excited states of [18]annulene may be predicted by using group theory arguments. As in the case of porphyrins<sup>8,9</sup> and related chlorins,<sup>1</sup> the absorption spectrum may be explained in terms of a four-orbital model (Hückel approximation), *i.e.*, by the promotion of an electron from the top-filled pair of orbitals ( $e_{2u}$ ) to the lowest empty orbitals ( $e_{1g}$ ). The over-all ground-state configuration  $a_{2u}^2 e_{1g}^4 e_{2u}^4 b_{1g}^2 b_{2g}^2 e_{2u}^4$  belongs<sup>26</sup> to the symmetry species  $^1A_{1g}$ ; on the other hand, the new symmetry after the transition of an electron becomes  $A_{1g} \times e_{2u} \times e_{1g} = E_{1u} + B_{1u} + B_{2u}$ <sup>27</sup> and this accounts for three absorption bands. The transition  $^1A_{1g} \rightarrow ^1E_{1u}$  is allowed (band I seen in 0-0 transition)<sup>25a</sup> whereas the two transitions  $^1A_{1g} \rightarrow ^1B_{1u}, ^1B_{2u}$  are forbidden (although partially allowed through a vibrational process). Use is made of Moffitt's result on intensity borrowing<sup>29</sup> to assign band II to the 0-1 vibrational component of the  $B_{1u}$  state, whereas the components of the  $B_{2u}$  band are likely to occur between 400 and 500 nm<sup>25a</sup> or at higher wavelength.<sup>27</sup> The correspondence between group theory nomenclature and other notations<sup>30,31</sup> is shown in Table IV. It is very pertinent for our purpose to note that among the various ground and excited states, only  $^1E_{1u}$  is degenerate and should lead to a non-zero  $A$  value.

Table IV. Nomenclature of Excited States for [18]Annulene

Group theory	Clar <sup>a</sup>	Platt <sup>b</sup>
$B_{1u}$	$p$	$^1L_a$
$B_{2u}$	$\alpha$	$^1L_b$
$E_{1u}$	$\beta$	$^1B$

<sup>a</sup> From ref 30. <sup>b</sup> From ref 31.

The same qualitative explanation probably holds also for the case of the (almost) planar 1,7,13-tridehydro[18]annulene (the degenerate state being actually  $^1E'$  in the D<sub>3h</sub> point group) and of the heterocyclic analogs of [18]annulene. These latter systems have 24  $\pi$  electrons,<sup>32</sup> of which 18 come from the ring carbons as in the case of the parent compound. As the Hückel approximation only accounts for adjacent atom

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interactions,<sup>33</sup> it is expected that the reduction of the symmetry from  $D_{6h}$  to  $D_{3h}$  (and possibly lower in the trisulfide) would not modify the qualitative interpretation of the spectra. The location and intensity of the bands, however, should reflect this lowering of the symmetry.

In molecules possessing no threefold axis of symmetry, theory predicts that the degeneracy of the excited state corresponding to the strong band is lifted. Considering *trans*-15,16-dimethyldihdropyrene (IX) as an example, the  $E_{1u}$  state predicted in the  $D_{14h}$  point group (perimeter model) leads to the  $B_{3u}$  and  $B_{2u}$  (or  ${}^1B_a$  and  ${}^1B_b$  in Platt's notations)<sup>31</sup> states in the  $D_{2h}$  point group.<sup>34</sup> As a result, two absorption bands occur. The theory of MCD then predicts two  $B$  terms of opposite sign<sup>4</sup> and this is in good agreement with our data (peaks observed at 333 and 372 nm in Figure 9).

The cases of [8]annulene (XII) and [16]annulene (XI) should probably be considered separately. For planar neutral  $C_{4n}H_{4n}$  cyclic systems having a threefold or greater axis of symmetry, Hückel's theory<sup>35,36</sup> predicts a pseudo-degenerate ground state, which should give rise to a  $C$  term in MCD measurements. Since these two molecules are known to be nonplanar,<sup>14</sup> the assumption of a  $C$  term existing in planar  $C_{4n}H_{4n}$  systems cannot be checked. It must be pointed out however that in XI the  $A/D$  ratio for the strong band (at 284 nm) has been shown experimentally to be zero or very small (actually a possible S-shaped curve was not detected with our apparatus), a result which seems to support *no degeneracy*, either in the *ground* or *excited* state of this molecule.

#### 4. Comparison between Theory and Experiment.

It follows from the arguments given above that the ground state of  $(CH)_{4n+2}$  hydrocarbons and their derivatives is totally symmetric and nondegenerate. Therefore  $C$  is zero and only  $A$  and  $B$  terms may occur.

Confining ourselves to compounds of higher symmetry, we have calculated  $A/D$  for [18]annulene (II), [18]annulene trioxide (III), [18]annulene dioxide sulfide (IV), and tridehydro[18]annulene (I), which are (almost) planar and lead to unambiguously S-shaped MCD curves (see Figure 12 where the abscissa scale has been extended and the ordinate scale has been reduced). Use was made of the previously described technique and our results are summarized in Table II. The value of  $\Gamma$  has been estimated roughly from the absorption curve and the resulting error may be of the order of 10%. The  $B/D$  ratio was calculated for sake of completeness but it is likely to be only a rough estimate, owing to some overlapping vibrational bands. The S-shaped dispersion curve observed for the stronger band (288 nm) in the nonplanar trisulfide (Figure 6b) would tend to support a degeneracy or near-degeneracy

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(36) See ref 32, p 2299.

of the corresponding excited state. The spectrum of the disulfide oxide (Figure 6a) seems much more complex and the above-described technique failed in analyzing it as an unambiguous linear combination of  $A$  and  $B$  terms (or  $B$  terms alone). It can be tentatively assumed, however, that absorption components of different polarization have to be invoked to explain the features of the MCD spectrum between 330 and 250 nm.

It is not our purpose here to calculate  $A/D$  ratios by quantum mechanical methods. It should be pointed out, however, that this has been done<sup>10</sup> recently in the case of coronene and triphenylene ( $D_{6h}$  and  $D_{3h}$  symmetry, respectively) and that the results have strong theoretical support. If vibronic interactions are absent (if present, they would lead to some quenching of the orbital angular momentum)<sup>37,38</sup> and the Franck-Condon approximation is adopted, one obtains  $\mu = -2A/D$ , where  $\mu$  is the magnetic moment of the excited state<sup>6</sup> ( ${}^1E_{1u}$  or  ${}^1E$ , according to the symmetry). On the other hand,  $\mu$  is expressed as the sum or the difference of two matrix elements which themselves may be positive or negative. As a result,  $\mu$  may be either positive or negative and relatively large or very small.

In the case of compounds of lower symmetry (*e.g.*, VII and X) no attempt has been made to extract the  $B/D$  parameter from our experimental curves, although this can be done by the use of the above-described technique.

The present studies have demonstrated the great dependence of the  $A/D$  ratio (and therefore the magnetic moment between a pair of degenerate excited states) upon the structure of the molecule under consideration and they have shown that this ratio may either be positive or negative. It is worth noting that the sign observed for [18]annulene (II) is different from the one determined for zinc hematoporphyrin<sup>8</sup> or other metal porphyrins<sup>8</sup> which possess the same basic 18-membered ring system.

We realize that, at this stage, advanced theoretical studies are indicated but it is our hope that our numerical results, while admittedly approximate, will stimulate such work; they should also assist in checking various molecular orbital treatments and in shedding light on the extent of vibronic quenching present. In addition, our results at longer wavelengths are likely to provide information about the vibrational process through the forbidden absorption bands.

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