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THE OPTICAL ACTIVITY OF CHROMOPHORES OF SYMMETRY C_2

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Abstract— Much evidence points to the fact that the long-wavelength part of the CD spectrum of chromophores of symmetry C_2 and of well-defined chirality exhibit certain common features. Calculations on a wide variety of systems predict that if the sense of screw is righthanded transitions of symmetry A will in general lead to negative Cotton-effects, transitions of symmetry B to positive ones. This apparent regularity is critically discussed for a number of different molecules and in relation with various computational approaches.

INTRODUCTION

THE CONDITION for optical activity in molecules is the absence of a plane of symmetry or a centre of inversion. Molecules of point group symmetries containing only axes of rotation are therefore optically active, the simplest case being C_2. In such molecules all transitions belong either to the irreducible representation A or B. In the first case they are polarized parallel to the twofold symmetry axis, in the second case perpendicular.

Molecules of symmetry C_2 may conveniently be viewed as composed of two equivalent parts. If the coupling between these two parts is relatively weak an exciton model may be applied to describe the resulting long-wavelength transitions, which are viewed as combinations of two local excitations. One resulting transition is of symmetry A, the other of symmetry B and the rotational strengths are opposite in sign.[1] If, on the other hand, the coupling between the two fragments is strong, the whole chromophore must be considered as inherently dissymmetric. A description by molecular orbitals extending over the complete chromophore is more suitable. A wide variety of LCAO-MO calculations, including configuration interaction, tend to show that a similar pattern is predicted for the long-wavelength part of the spectrum as in the exciton model.

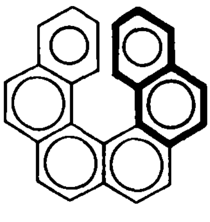
C_2 is the point group symmetry of a regular helix, the twofold symmetry axis lying perpendicular to the helical axis. Whenever a definite helicity may be attributed to a chromophore we have noticed the following concerning the longest-wavelength part of the spectrum. When the sense of screw is right-handed transitions of symmetry A tend to show negative Cotton-effects, transitions of symmetry B positive ones. This result may be visualized by considering the nodal properties of the wave-functions.[2] It must be emphasized that we refer exclusively to the sense of screw of the chromophore itself, which must not necessarily be identical to the one of the underlying molecular frame. To determine the chirality, a chromophore is visualized in the energetically most easily accessible planar conformation of effective C_{2v} symmetry. The C_2-axis lies in this plane and it divides the plane into a right part and a left part. The molecule (chromphore) is then twisted into its assumed real conformation. If the right-hand part of the molecule (chromophore) is twisted counterclockwise, the left part clockwise, then the chirality is right-handed.

We present here a survey of some well-known chromophores of symmetry C_2 and critically discuss the above-stated regularity. Beside an eventual stereochemical applicability of such a rule there is the spectroscopic interest of directly correlating Cotton-effects with the direction of polarization of electronic transitions.

A general survey

(a) *From dienes to helicenes.* Both HMO calculations[3] as well as more elaborate computations[4] show that in a twisted diene (I), be it closer to *cis* or to *trans*, a transition of symmetry B appears at longest wavelength, followed by a transition of symmetry A. These predictions are in agreement with experiment. For a right-handed diene the first Cotton-effect is positive, followed by a negative one. Exceptions to the diene rule[5] must be attributed to strong interaction with neighbouring substituents, which destroys the effective C_2 symmetry or the effective sense of chirality (see also section 3). In the much larger chiral conjugated systems, the helicenes (II), a general pattern not dissimilar to that of the *cisoid* dienes is encountered. However, it only clearly emerges as the result of explicitly considering electron interaction. From PPP calculations invoking configuration interaction for right-handed helicenes one predicts with increasing energy a number of strong positive Cotton-effects, which are predominantly of symmetry B, followed by some opposite ones of symmetry A.[6] This leads to the conclusion that right-handed helicenes should have positive long-wavelength optical activity.[6, 7] Recently the absolute configuration of a hetero-helicene has been established by X-ray analysis.[8] It shows that the (+)-isomer should have right-handed (or P) configuration. One may safely assume the molecule in question to strongly resemble hexahelicene in its electronic structure.[*] It gives strong support to the predicted absolute configuration of hexahelicene. Very recently Martin has proven by chemical means that (−)-hexahelicene indeed has the left-handed (or M) configuration.[9]

I



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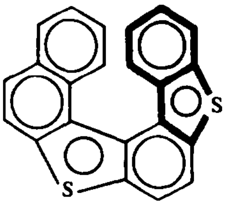


III

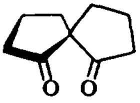
(b) *Diones.* CNDO-CI calculations on a twisted glyoxal molecule[10] predict a transition of symmetry B to appear at longest wavelength in the *cisoid* case. As the molecule gets twisted to *trans* this transition moves backward and a transition of symmetry A appears at lowest excitation energy which entails a change in the sign of the predicted first Cotton-effect. Experimental data on the optical activity of diones is not very abundant. In 2,3-camphorquinone[4] one may assume that the dicarbonyl

[*] Spectroscopically in a conjugated system a sulphur atom may sometimes act as a double bond.

chromophore has a *cisoid* left-handed twist through steric interference with the bridgehead methyl group. The experimental longest-wavelength Cotton-effect is negative in accord with the predictions of the twisted glyoxal model. Measurements of the polarization of this transition by the method of electrochromism[11] confirm that it is polarized perpendicular to the molecular dipole moment, which implies the symmetry B.

IV

(c) *Some spiro compounds.* (+)-(5R)-spiro[4.4]nonane-1,6-dione[12] shows a positive Cotton-effect at 315 nm and a negative one at 287 nm. The chromophore being known to be right-handed from chemical evidence, the first transition must be of symmetry B, the second one of symmetry A, by the C_2-rule. The results of CNDO calculations support this conclusion.[4]



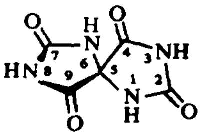
V

VI

VII

In homoconjugated dienes of type VI and VII the two π → π* transitions are calculated to be nearly degenerate. In both cases a transition of symmetry B should lie lowest, immediately followed by one of symmetry A. CNDO-CI calculations for the recently synthesized[13] (5R)-spiro[4.4]nonane-1,6-diene predict a large negative Cotton-effect for the A-transition and a smaller positive one for the B-transition. A superposition of both Cotton-effects would lead to a negative resultant. The measurement seems indeed to reveal such a spectrum.[14] The rotational strength deduced from the longest-wavelength CD-band agrees well with the sum of the calculated values.

Both enantiomers of spirobihydantoin (VIII) were recently separated.[15] However, a determination of the absolute configuration did not immediately appear to be possible. One may assume that the long-wavelength part of the CD-spectrum depends predominantly on the two carbonyl groups in the 4- and 9-positions. The carbonyl groups in the 2- and 7-positions should play a secondary role for the long-wavelength optical activity of the compound, as their surroundings are analogous to the ones in derivatives of urea, where n → π* transitions appear below 210 nm.

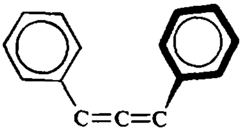


VIII

The similarity of VIII to V leads one to assume that the long-wavelength part of the CD-spectra resemble each other. The spectrum of VIII should lie more to the blue, corresponding to the amide character of the active chromophores. A transition of symmetry B should appear at longest wavelength, followed by a transition of symmetry A. In a left-handed molecule or chromophore, the former Cotton-effect should[11] be negative, the latter positive.

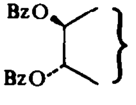
Experimentally (−)-spirobihydantoin shows in THF a negative Cotton-effect at 250 nm ($\Delta\varepsilon \approx -1$) and a positive one at 232 nm ($\Delta\varepsilon \approx +1{\cdot}5$). One would therefore conclude that the absolute configuration of the molecule is given by VIII.

(d) 1,3-*Diphenylallene.* Mason and Vane[16] have studied (+)-1,3-diphenylallene with the exciton model. They interpret the two Cotton-effects at 254 nm and 232 nm, the first one being positive, the second one negative, as arising from transitions of respective symmetry B and A. The chromophore is right-handed.



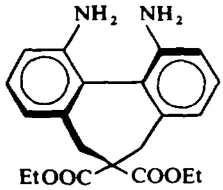
IX

(e) *The dibenzoate-rule.* Recently Harada and Nakanishi[17] have deduced a chirality rule for dibenzoate. Benzoate shows at about 230 nm an absorption which is ascribed to a $\pi \rightarrow \pi^*$ transition polarized along the long-axis of the single chromophore. In a dibenzoate as shown in X one obtains by the exciton model an A and B transition. The latter is expected to appear at greater wavelength. Harada and Nakanishi have found experimentally that of the two Cotton-effects appearing near 230 nm in a dibenzoate of right-handed chirality the longer-wavelength one is always positive, the shorter-wavelength one always negative.

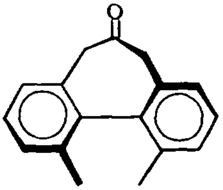


X

(f) *Biphenyls and related compounds.* Among the many biphenyl derivatives which have been investigated[18] we pick out some cases where the polarization of one or more transitions may be deduced with a high degree of certainty.



XI

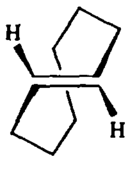


XII

In XI the longest-wavelength Cotton-effect is positive. From the analogy to the aniline spectrum and from the exciton model, or from PPP-calculations the transition is predicted to be of symmetry B.

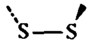
The exciton model cannot be applied to predict the sign of the longest-wavelength Cotton-effect in XII, attributable to a transition of the $n \rightarrow \pi^*$ type. The absolute configuration of XII was established from ORD data by analogy with other β,γ-unsaturated ketones, in the frame of an extension of the octant rule.[19] The transition in question being undoubtedly of symmetry A, the corresponding Cotton-effect must be negative by the C_2-rule, which is indeed the case.

(g) trans *Cycloöctene.* The chirality of *trans* cycloöctene is determined by viewing the bonds adjacent to the double-bond as part of the chromophore. In Fig XIII the chromophore is twisted in a right-handed way out of an imaginary planar *cis* conformation, defining a plane in which the C_2-axis lies.



XIII

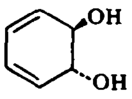
CD measurements[20] seem to indicate that there is more than one Cotton-effect of the same sign in the 180–220 nm region. From a theoretical standpoint it appears that the corresponding transitions probably are of the type $\pi_z \rightarrow \pi_z^*$ and $\pi_z \rightarrow \pi_y^*$, the first transition being electric dipole allowed in planar ethylene, the second one magnetic dipole allowed. In the twisted chromophore both transitions are of symmetry B. By the C_2-rule they should therefore both lead to positive Cotton-effects. This would agree with experiment. However, it is not entirely in accord with some more detailed calculations.[21]



XIV

(h) *Organic disulfides.* Michl and Linderberg[22] have theoretically studied the twisted disulfide chromophore. They find in the *cisoid* case an excited state of B-symmetry to lie lowest, in the *transoid* conformation an excited state of A-symmetry. The model which they consider has left-handed chirality, leads to the prediction that the longest-wavelength Cotton-effect should be negative in the first case and positive in the second. In XIV, where the chirality is right-handed, the signs would be reversed.

(i) *Further examples.* For (−)-(1R,2R)-*trans*-1,2-dihydro-1,2-dihydroxy-benzene[23] (XV) Dreiding models predict two possible conformations: The hydroxyl groups are either both quasi-equatorial or quasi-axial. In the first conformation the diene-system appears from the models to have a slight right-handed twist. If one assumes the chromophore to consist of the diene plus the two hydroxyl groups, no definite chirality may be inferred. This conformation should probably be only slightly optically active. On the other hand, in the quasi-axial conformation the diene-plus-hydroxyl chromophore is definitely left-handed. Even if at room temperature the molecule oscillates quickly between the two conformations, the left-handed chirality should be the outweighing one for the long-wavelength optical activity.



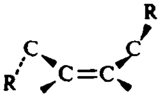
XV

Assuming the first transition to be basically of the diene-$\pi \rightarrow \pi^*$-type, it should be B-polarized. The corresponding Cotton-effect should then be negative, which is indeed the case experimentally.

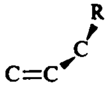
To mention a further chromophore of effective symmetry C_2, which however has only partly been investigated spectroscopically, the urobilins[24] may exist in a tight helical form, stabilized by internal hydrogen bonding and showing very strong Cotton-effects. PPP-type calculations of the lower electronic transitions, combined with an extensive recording of the CD spectrum should be of interest in connection with the C_2-rule.

DISCUSSION

(a) *The allylic axial bond effect.* It appears that allylic axial bonds may play a decisive role in determining the sign of the long-wavelength Cotton-effects in olefins.[25] It is, as if the double bond plus the axial bonds form a single chromophore. From the C_2-rule one would expect XVI to be right-handed and to show a positive Cotton-effect for the B-polarized $\pi_z \rightarrow \pi_z^*$ transition. If the influence of the axial bonds is roughly additive, the same should hold for XVII, which may be viewed as pseudo C_2 symmetric.



XVI



XVII

The point of view of the C_2-rule is justified as long as the double bond may unambigously be viewed as part of an inherently dissymmetric chromophore of definite chirality. In general, the C_2-rule does not lead to a sector rule for a particular transition. In the case, however, where the contributions of single allylic bonds to a Cotton-effect are considered separately, as in XVII, one arrives of course at an octant rule. This is in accord with the work of Schellman[26] who predicts an octant rule for an asymmetrically perturbed chromophore of effective symmetry D_{2h}. Whenever discrepancies with the results of the C_2-rule, as applied to the molecule as a whole, occur they may be attributed to the existence of several locally opposed senses of chirality. Consequently the sense of screw of the whole system may be considered as ill-defined. It should be noted that our type of argument is similar to that used previously by Burgstahler and Barkhurst for dienes.[5] These authors break the system up into partial subchromophores in the same way.

Recently Scott and Wrixon[27] have developed an octant rule for asymmetrically perturbed monoolefins. The signs they attribute to the different octants are at variance with those derived from XVII. However, they do not take into account allylic hydrogen atoms as substituents in their work. If allylic C—H-bonds are considered to play a more important role in determining the chirality of the olefin chromophore than C—C-bonds and if they are given the sign of XVII, the apparent discrepancy is resolved in many cases.

It appears that in heteroannular *cisoid* conjugated dienes and enones allylic axial interaction may override the conjugative coupling of the two double bonds, leading to Cotton-effects of sign opposite to the ones expected by solely considering the diene or enone chromophore.[5]

(b) *Helical polymers.* In a regular helix transitions polarized parallel to the helical axis are always of symmetry B, transitions polarized perpendicularly are either of symmetry A or B. Recent investigations of helical polymers by the exciton model[28] have shown that in the first case all Cotton-effects of an exciton band should have the same sign, whereas in the second case both positive and negative Cotton-effects are to be expected. If the effective sense of screw of the chromophore is right-handed this would, by the C_2-rule, imply that negative Cotton-effects correspond to transitions of symmetry A and that these transitions consequently are polarized perpendicular to the helical axis. The predictions by Tinoco's and Woody's model of a free electron on a helix[29] are in accord with these conclusions. However, the validity of the C_2-rule for "infinite" helices is still a matter of further investigation.

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