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INFLUENCE OF SUBSTITUTION PATTERN ON THE BENZENOID TRANSITIONS:

QUANTITATIVE EVALUATION OF THE ELECTRONIC AND VIBRATIONAL COMPONENTS FROM NEW EXPERIMENTAL POLARIZATION DATA

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Abstract—The influence of substitution on the benzenoid ^1L_b, ^1L_a and ^1B transitions is studied by the technique of linear dichroism in stretched polyethylene films.

The total intensity of the ^1L_b system is resolved into induced and vibrational components and the influence of various substitution patterns on the magnitude and polarization of both components is analyzed quantitatively. As expected from theoretical considerations, the vibrational components like the induced intensity are found to be strongly affected by the substituent strength and the symmetry of substitution pattern. The previously accepted assumption, according to which the vibrational intensity is regarded as a constant, appears to be completely unrealistic when dealing with cases of strong substituents. A satisfactory quantitative treatment of both weak and strong substituents using the same simple theoretical approach seems possible only if the systematic variations observed in the vibrational intensity are not neglected.

A qualitative analysis is given for the ^1L_a and ^1B systems. The results are compared with available theoretical predictions and previous experimental data.

Practical implications of the present new experimental information to the study of aromatic optical activity are discussed.

The theory of Sklar[1] and Petruska[2] has been widely checked with respect to its predictions regarding the intensity of the ^1L_b system and the frequency shifts of both ^1L_b and ^1L_a systems on substitution.[1-4]

Much less experimental data is available for the confirmation of the predictions concerned with the directions of polarization imposed by different substitution patterns on the benzenoid transitions. Most of the previous polarization measurements have been carried out on highly symmetric benzene derivatives in the crystalline state.[5-9] Davydov splitting complicates considerably the interpretation of such data and technical problems do not permit the extending of the measurements in crystals to short wavelengths. The techniques of photoselection and incorporation of molecules in stretched polyethylene films were applied only to the special cases of a few *mono* and *para*-disubstituted benzene derivatives.[5,6,10]

The present investigation deals with the use of linear dichroism (LD) in stretched polyethylene films for the purpose of studying the influence of various substitution patterns on the polarization of benzenoid transitions. This technique, which has been developed to a quantitative level in our laboratory,[15,16] provides more subtle experimental information, unobtainable from intensity or frequency shifts measurements only. It thus becomes possible for the first time to analyze the influence of substitution on the vibrational intensity of the ^1L_b system. In addition, the present polarization data allow the extending of experimental efforts towards the study of the strong ^1L_a and ^1B transitions, for which the small expected intensity changes could not be properly measured.[1-3] Utilizing steroids as convenient carrier molecules[15,16] it becomes possible for the first time to orient in a known predestinated direction also unsymmetrically substituted benzene derivatives and to establish their directions of polarization.

Recent circular dichroic studies of chiral aromatic compounds have stressed the importance of knowing the directions of the electric transition moments for determinations of absolute configuration.[11-14]

A new approach to the interpretation of the circular dichroism of substituted benzene chromophore, based on accurate polarization data available from LD measurements in stretched polyethylene films, will be presented in a following publication.[17]

TREATMENT OF LD DATA

A model of orientation which correlates the measured dichroic ratio $d_0(\lambda)$[18] with two molecular properties, the orientation parameters f and the angle α between the transition moment vector and the molecular axis of orientation, has been previously developed.[15,16]

The model may be applied to elongated, disk-like and planar shortened molecules, oriented in stretched polyethylene matrices.[19] We have measured the LD spectra of a series of substituted benzene derivates incorporated in stretched polyethylene matrices. These data, expressed as dichroic ratios, have been used to resolve the UV spectra into components polarized along orthogonal directions, related to molecular coordinates.[15,16] The resolved spectra thus obtained are analyzed in terms of Sklar theory. We follow the method of spectroscopic moments developed by Platt.[3] According to Platt, the transition moment induced by a certain substitution pattern is a resultant vector obtained by summing the spectroscopic moments induced by each substituent.

Assuming the additivity of induced and vibrational intensities,[1,2,5,6] one writes

$$I = I_v + I_i \tag{1}$$

$$I_i = \mathbf{m}_i^2, \tag{2}$$

where I_v is the vibrational intensity, I_i the induced intensity, $\mathbf{m}_i$ the resultant induced transition moment vector and I the total transition intensity. The total transition intensities are conveniently approximated by the maximum extinction coefficients, $\epsilon(\text{sm})$, obtained from the smoothed extinction curves.[3] It follows from eqn (1) that:

$$\epsilon(\text{sm}) = \epsilon_v(\text{sm}) + \epsilon_i(\text{sm})$$

$$\epsilon_i(\text{sm}) = \mathbf{m}_i^2, \tag{3}$$

where $\epsilon_v(\text{sm})$ and $\epsilon_i(\text{sm})$ are the maximum extinction coefficients obtained from the vibrational and the induced extinction curves, respectively.

In general, it is expected that the vibrational and induced curves will show a different wavelength dependence, which may be detected by polarization measurements. Experimentally, this fact is revealed by the dependence of d_0 on λ. In most of the LD spectra measured by us d_0 is a strongly varying function of λ.

The dependence of d_0 on λ may be conversely expressed as a dependence of α on λ.[19] Since vector addition of the induced and vibrational transition moments which are polarized in different directions does not occur,[6] and since in symmetrically substituted benzenes these directions are well defined by strict selection rules,[5,6] it follows that $\alpha(\lambda)$ represents in fact only an effective angle which reflects the different wavelength dependence of the induced and vibrational extinction curves. In cases in which $\epsilon_v(\text{sm}) = 0$, α takes on a constant value, characteristic of the induced moment direction.

Let us consider the case of a substituted benzene where the induced transition moment makes an angle γ with the molecular orientation axis, which is supposed to lie in the plane of the chromophore. If there are no out-of-plane vibrational components and assuming that the in-plane vibrational transition moments are constrained by symmetry to point only in directions parallel or perpendicular to the induced moment,[6] the following equations may be derived:

$$\epsilon(\text{sm}) = \epsilon(\text{sm})_\parallel + \epsilon(\text{sm})_\perp \tag{4}$$

$$\epsilon_v(\text{sm}) = \epsilon_{vi}(\text{sm}) + \epsilon_{vv}(\text{sm}) \tag{5}$$

$$\begin{aligned} \epsilon(\text{sm})_\parallel &= \epsilon(\text{sm})\cos^2\bar{\alpha} = [\epsilon_i(\text{sm}) + \epsilon_{vi}(\text{sm})]\cos^2\gamma \\ &\quad + \epsilon_{vv}(\text{sm})\sin^2\gamma \\ \epsilon(\text{sm})_\perp &= \epsilon(\text{sm})\sin^2\bar{\alpha} = [\epsilon_i(\text{sm}) + \epsilon_{vi}(\text{sm})]\sin^2\gamma \\ &\quad + \epsilon_{vv}(\text{sm})\cos^2\gamma \end{aligned} \tag{6}$$

where $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ are the maxima of the smoothed extinction curves polarized in directions parallel and perpendicular to the orientation axis, $\epsilon_{vi}(\text{sm})$ and $\epsilon_{vv}(\text{sm})$ represent the vibrational components polarized parallel and perpendicular to the induced moment direction, respectively, and $\bar{\alpha}$ is an average α angle defined by eqns (4)–(6).[21]

Now, the parameters of interest appearing in eqn (6) are of course γ, $\epsilon_i(\text{sm})$, $\epsilon_{vi}(\text{sm})$ and $\epsilon_{vv}(\text{sm})$, but only $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ may be directly derived from the LD data.

We have determined $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ by the following method: using the experimental $d_0(\lambda)$ and f values, the UV isotropic extinction curves were resolved into components polarized parallel and perpendicular to the molecular orientation axes.[16,19,21] The total transition intensity and the component intensities were compared by measuring the integrated extinction coefficients corresponding to each curve. $\epsilon(\text{sm})$ was directly estimated from the isotropic smoothed extinction curve, while $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ were obtained multiplying $\epsilon(\text{sm})$ by the relative contributions of each component to the total integrated transition intensity. This procedure ensures a higher accuracy, as only one extinction curve has to be smoothed by eye, while the relative contributions of each component are determined by exact integration. It is important to emphasize at this point that the polarized as well as the isotropic extinction curves were derived from the same stretched film sample.[16] The relative magnitudes of $\epsilon(\text{sm})$, $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ are therefore obtained from measurements performed on the same molecular assembly. Their absolute values however refer to measurements of $\epsilon(\text{sm})$ in hexane solutions. A direct analogy between the spectral properties of molecules dissolved in polyethylene and in a liquid hydrocarbon solution seems entirely justifiable in this case, as the spectra taken in both media were practically identical.

The determination of γ, $\epsilon_i(\text{sm})$, $\epsilon_{vi}(\text{sm})$ and $\epsilon_{vv}(\text{sm})$ from the $\epsilon(\text{sm})_\parallel$ and $\epsilon(\text{sm})_\perp$ values necessitates further assumptions, which will be discussed in connection with each of the specific examples to be presented in the following.

MEASUREMENTS AND THE MOLECULAR ORIENTATION IN STRETCHED POLYETHYLENE

The LD measurements include 17 compounds containing different substituted benzene chromophores: *para*-dimethylbenzene (P-xylene), *para*-dimethoxybenzene (DMB), N,N',N,N' - tetramethyl - p - phenylene diamine (TMPD), *para*-dimethylterephthalate (DMTP), *trans-p-t*-butylcyclohexyl anisate (TBCA), hexamethylbenzene (HMB), 1,3,5-trimethylbenzene (TMB), 1,2,4,5-tetramethylbenzene (durene) (see Figs. 2–8), and 9 androstane steroids with aromatic A or B rings (Fig. 1).

All compounds were carefully purified by chromatographic methods, repeated crystallization and zone-refining. The LD spectra were recorded at room temperature with a Cary-15 spectrophotometer purged with nitrogen, using the waveplate or the PNP methods.[15,16]

The first five compounds and the steroids are classified as elongated molecules, TMB and HMB as disk-like molecules, and durene may be considered to fall in the group of shortened molecules.[19] The axes of orientation are, according to our model, the longitudinal molecular axes for the cases of elongated and shortened molecules and the symmetry axes perpendicular to the molecular planes for disk-like molecules.[15,16]

The preferred conformation of the OMe groups in DMB is probably *trans*,[22] implying that the longitudinal molecular axis makes an angle of *ca.* 20° with the line passing through the *para*-C atoms. Similar geometrical considerations show the longitudinal axis of DMTP to be inclined at an angle of *ca.* 10° with respect to the line passing through the *para*-C atoms. Since the deviation of

TMPD from exact D_{2h} symmetry is probably small,[6] its longitudinal axis is considered to pass through the N atoms.

The orientation of compounds possessing androstane skeletons have been previously established[15,16] (Fig. 1).

Determination of f parameters

The LD spectra of DMB, TMPD, DMTP and TBCA show intense ^1L_a bands with high d_0 values. These bands have an allowed character and are supposed to contain appreciable charge-transfer contributions.[2,6,28] It is therefore reasonable to assume that the maximum d_0 values, which are invariably reached in the 0–0 region of the ^1L_a bands, correspond to single transitions polarized along the line passing through the *para*-C atoms. This assumption allows the orientation f parameters to be calculated[23] (Table 1).

The f parameter of P-xylene cannot be obtained from the ^1L_a band, which still has a forbidden character in this compound. We have observed that in many cases, in particular those of weak substitution, the allowed strong ^1B band keeps its degenerate character, being polarized in plane with components of approximate equal magnitude in each direction. The moderate and constant d_0 value over the entire ^1B band of P-xylene is characteristic of such a behaviour. The f parameter of P-xylene was thus calculated assuming an angle $\alpha = 45°$ corresponding to the d_0 value of the ^1B band.[19]

Durene has molecular dimensions similar to those of naphthalene. It may be assumed that the orientation in polyethylene of both compounds is also similar. Identical f values with those of naphthalene[16] were adopted as orientation parameters for Durene (Table 1).

The f's of the steroid compounds have been previously determined.[15,16]

The LD spectra of TMB and HMB show dichroic ratios which have constant values, greater than unity. This behaviour is typical of disk-like molecules oriented with their molecular planes parallel to the stretching direction of the film and having all transitions polarized in plane only[16,20] (see Fig. 2, for example).

Orientation f parameters for HMB and TMB were calculated for $\alpha = 90°$ corresponding to the measured d_0 values.[24]

It might be interesting to point out that in the case of elongated molecules the f parameters show a clear dependence on the molecular length (Table 1). The f parameter of HMB has a higher value than that of TMB, probably due to the fact the HMB better approximates a disk, while TMB has "empty corners".

Spectra resolved into components polarized parallel and perpendicular to the molecular orientation axes have been obtained using the $d_0(\lambda)$ and f values of each compound (Figs. 3–12 show typical examples of resolved spectra). In some cases it appeared convenient to change the directions of resolution, in accordance with the effective local symmetry of the chromophore (Figs. 4, 5 and 11).

DETERMINATION OF INDUCED AND VIBRATIONAL INTENSITIES

The ^1L_b system

HMB and TMB show no induced intensity and no out-of-plane vibrational components, $d_0(\lambda)$ assuming a constant value over the entire spectrum. This result is in full agreement with theory. Although, due to steric strain, HMB is somewhat distorted from perfect planar geometry, no out of plane component could be detected[25] (Fig. 2). It can therefore be safely assumed that all the intensity of the ^1L_b and ^1L_a transitions is vibrationally borrowed from the strong ^1B band. According to eqn (3)

$$\text{For HMB and TMB}\begin{cases} \mathbf{m}_z = 0 \\ \epsilon_v(\text{sm}) = \epsilon(\text{sm}) \end{cases} \qquad (7)$$

The vibrational intensity borrowed from the degenerate ^1B band has two equal components polarized in orthogonal directions:[6]

$$\begin{matrix}\text{For HMB and}\\ \text{TMB}\end{matrix}\begin{cases} \epsilon_v(\text{sm}) = \epsilon_{vx}(\text{sm}) + \epsilon_{vy}(\text{sm}) \\ \epsilon_{vx}(\text{sm}) = \epsilon_{vy}(\text{sm}) = \frac{1}{2}\epsilon(\text{sm}) \end{cases} \qquad (8)$$

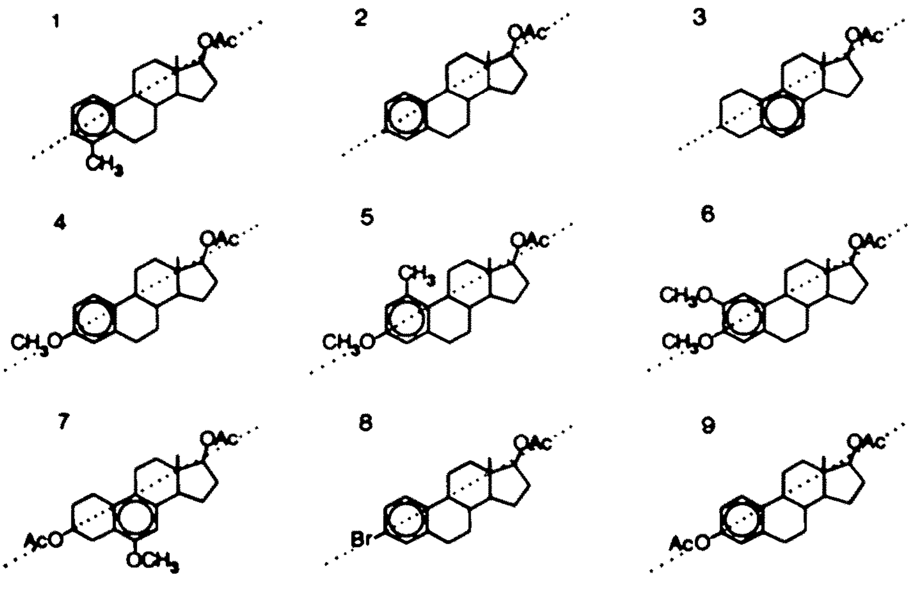

Fig. 1. The steroidal benzenes and their (· · · · · ·) axes of orientation in polyethylene.

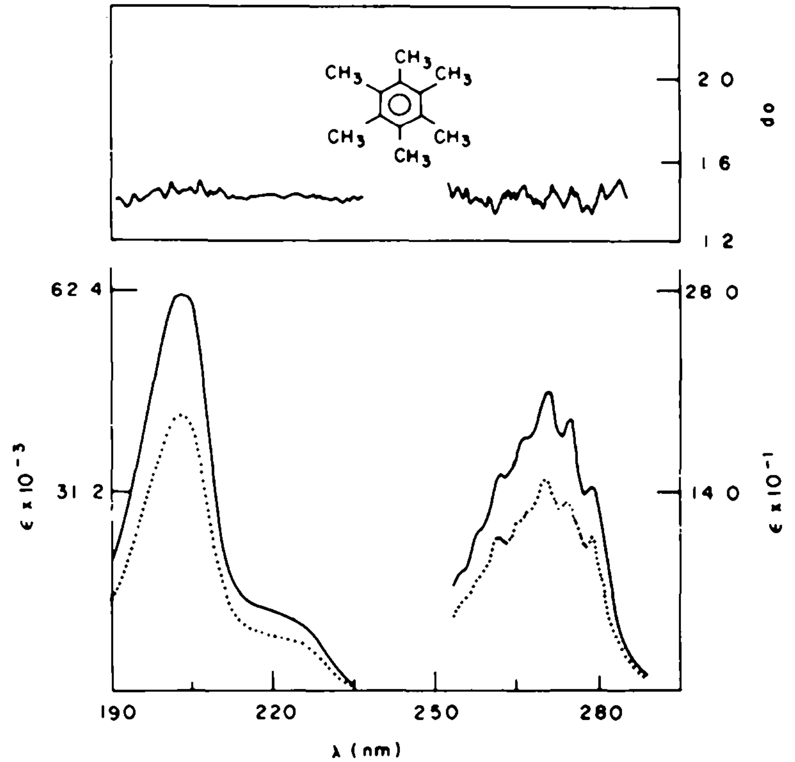

Fig. 2. LD spectrum of HMB: lower part, (· · · · ·) the extinction curve obtained by light polarized perpendicular to the direction of stretching; (——) the extinction curve obtained by light polarized in the direction of stretching; upper part, the plot of the dichroic ratios d_0 vs λ.

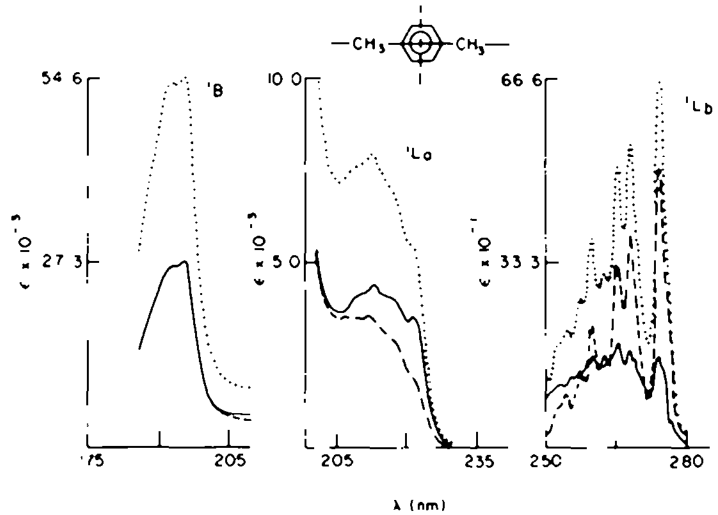

Fig. 3. Resolved spectrum of *para*-xylene: (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (-----) the short axis polarized component.

The small difference between $\epsilon(\mathrm{sm})_{\mathrm{HMB}}$ and $\epsilon(\mathrm{sm})_{\mathrm{TMB}}$ (Table 1) is probably due to the difference in the number of substituents only.

According to theory, the induced transition moments of the *para*-disubstituted benzenes (effective D_{2h} symmetry) are polarized in directions perpendicular and parallel to the line passing through the para C atoms for the ^1L_b and ^1L_a bands, respectively. Our LD measurements confirm this prediction (see Figs. 3–7). In addition to this, the ^1L_a band achieves allowed character also by mixing with transitions to a charge-transfer state.[2,6,28] The allowed character of the ^1L_a band increases with increasing strength of the substituents.[6]

It follows that the ^1L_b band may derive intensity also from the ^1L_a state and that this contribution must be polarized at 90° with the direction of the induced ^1L_b

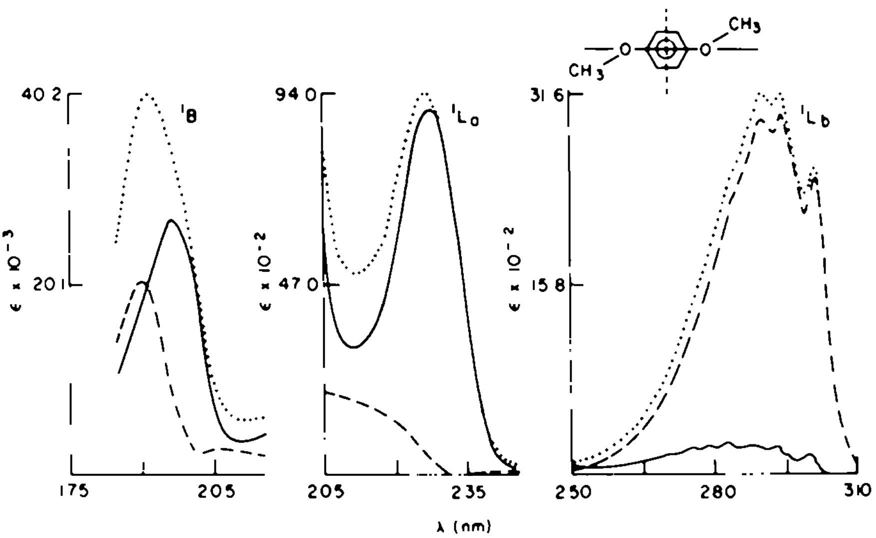

Fig. 4. Resolved spectrum of DMB: (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (- - - - -) the short axis polarized component.

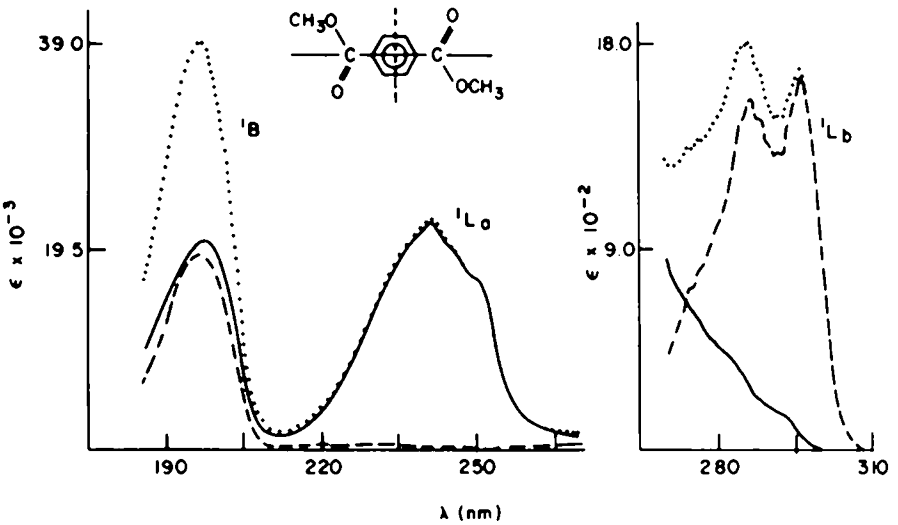

Fig. 5. Resolved spectrum of DMTP: (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (- - - - -) the short axis polarized component.

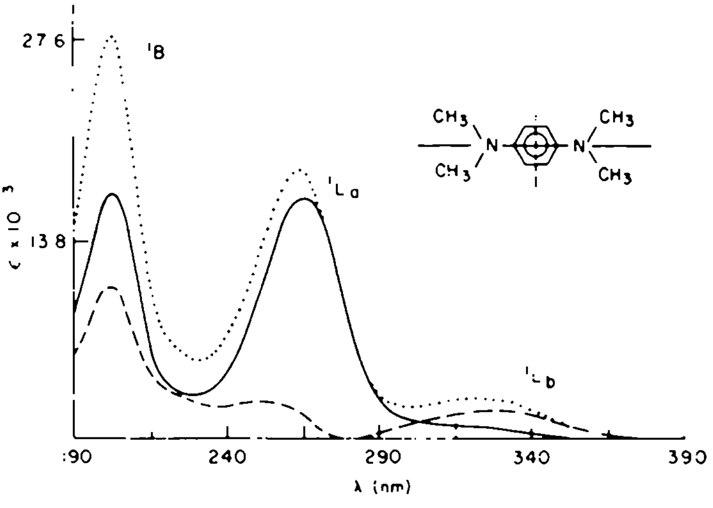

Fig. 6. Resolved spectrum of TMPD: (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (- - - - -) the short axis polarized component.

Table 1.

Compound	f	$\bar{\alpha}$ $(\alpha_{max}-\alpha_{min})^a$	ϵ^b(sm)	ϵ_i(sm)	ϵ_v(sm)	ϵ_{vv}(sm)	γ^c	β^c
TMB	−0.125	90° (90°–90°)	190	0	190	95	—	—
HMB	−0.235	90° (90°–90°)	206	0	206	103	—	—
P-xylene	0.244	50° (64°–30°)	420	155	265	170	90°	90°
Durene	0.334 0.438	34° (38°–32°)	635	335	300	200	0°	0°
DMB	0.30	63° (70°–50°)	3120	2705	415	320	70°	70°
DMTP	0.58	62° (80°–40°)	1670	1233	437	342	80°	80°
TMPD	0.22	57.6° (80°–43°)	2600	1765	835	740	90°	90°
Steroid 1	0.38	43° (46°–39°)	220	32	188	94	30°	—
Steroid 2	0.38	40.5° (43°–35°)	440°	191	249	154	30°	30°
Steroid 3	0.38	54.5° (56°–54°)	360	140	220	120	90°	90°
Steroid 4	0.39	62° (67°–51°)	2130	1710	420	325	73°	90°
Steroid 5	0.39	63.5° (72°–58°)	1920	1480	450	350	82.5°	90°
Steroid 6	0.39	37° (40°–30°)	3380	2510	870	770	30°	30°
Steroid 7	0.39	35° (39°–29°)	1560•	830•	730•	635•	7°•	30°
Steroid 8	0.38	32.5 (37°–30°)	720	260	460	365	42.5°	90°
Steroid 9	0.39	47° (49°–44°)	690	420	270	175	54.5°	90°
TBCA	0.59						90°	90°

[a] α_{max}, α_{min} are the extreme values of α over the band.
[b] ϵ(sm) is expressed in units of (cm.moles/liter)$^{-1}$.
[c] γ and β are measured relative to the orientation axis of each compound.
•Values calculated with the spectroscopic moments derived from the previous compounds in this Table.

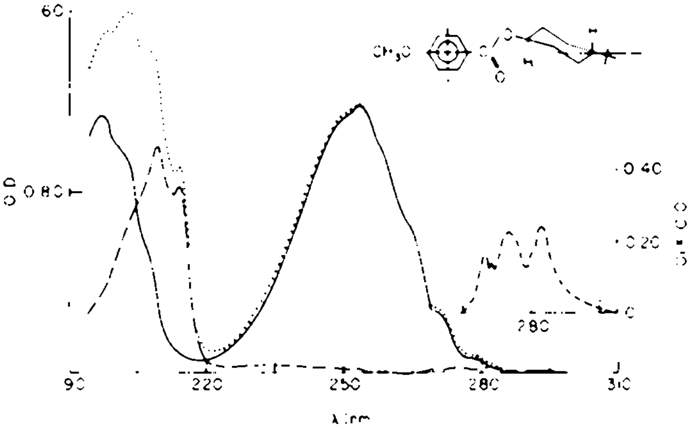

Fig. 7. Resolved spectrum of TBCA; (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (-----) the short axis polarized component.

transition moment. We assume that in all *para*-substituted benzenes

$$\epsilon_{vi}(\mathrm{sm}) \simeq \epsilon_{vi}(\mathrm{sm})_{\mathrm{TMB}} = \tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{TMB}}, \tag{9}$$

since this contribution is borrowed only from the strong ^{1}B state which, in general, does not change drastically on substitution, and

$$\epsilon_{vv}(\mathrm{sm}) \geqslant \tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{TMB}}, \tag{10}$$

since this part of the vibrational intensity contains contributions from both ^{1}B and ^{1}L$_a$ states.[26] The UV spectra of the *para*-disubstituted derivatives have been resolved into components polarized in directions parallel and perpendicular to the line passing through the *para* C atoms (Figs. 3–7). In this case eqns (6) reduce to:

$$\epsilon_a(\mathrm{sm}) = \epsilon_i(\mathrm{sm}) + \epsilon_{vi}(\mathrm{sm})$$
$$\epsilon_b(\mathrm{sm}) = \epsilon_{vv}(\mathrm{sm}) \qquad (11)$$

where $\epsilon_a(\mathrm{sm})$ and $\epsilon_b(\mathrm{sm})$ are obtained from the curves polarized in the directions of the induced moment and perpendicular to it, respectively. In P-xylene and TMPD the longitudinal symmetry axes of the chromophore and the orientation molecular axes coincide, so that $\epsilon_b(\mathrm{sm}) = \epsilon(\mathrm{sm})_{\parallel}$, $\epsilon_a(\mathrm{sm}) = \epsilon(\mathrm{sm})_{\perp}$ and $\gamma = 90°$.

From eqns (9), (10) and (11) it follows that

$$\epsilon_i(\mathrm{sm}) = \epsilon_a(\mathrm{sm}) - \tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{TMB}}, \qquad (12)$$

and according to eqn (2) the induced transition moment of *para*-disubstituted benzenes will be given by

$$|\mathbf{m}_i| = [\epsilon_a(\mathrm{sm}) - \tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{TMB}}]^{1/2} \qquad (13)$$

Similar symmetry considerations indicate that eqns (6) with $\gamma = 0°$ should be applied to Durene (Fig. 8). It was also assumed that $\tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{TMB}} < \epsilon_{vi}(\mathrm{sm})_{\mathrm{Durene}} < \tfrac{1}{2}\epsilon(\mathrm{sm})_{\mathrm{HMB}}$.

In the case of aromatic steroids, the plane defined by the benzene ring is very nearly identical with the best plane of the molecule. Since all benzenoid transitions are polarized in plane[27] and the orientation axis (Fig. 1) lies in the same plane,[15,16] it becomes possible to resolve the UV spectra of these compounds into components polarized along different in-plane directions. The spectra of steroids 2 and 6 (Table 1) have been resolved along directions determined by their local C_{2v} symmetry (30° and 60° with respect to the axis of orientation, as shown in Figs. 1 and 11). All other spectra have been resolved into directions parallel and perpendicular to the axis of orientation (Figs. 9, 10 and 12).

A somewhat ambiguous situation arises in the case of benzene derivatives with low local symmetry (C_s), since the vibrational intensity of these compounds cannot be resolved into independent components, polarized along well defined orthogonal directions. However, it proved feasible to resolve it into directions keyed to the position of the most effective substituent. This approximation is compatible with the observation that in the presence of a strong substituent the ^1L_a system acquires allowed character and becomes polarized approximately in the direction of the bond axis of that substituent. Consequently, the ^1L_b band should gain vibrational intensity in the same direction. In the absence of strong substituents the vibrational intensity of ^1L_b band, derived mostly from the ^1B state, is isotropically polarized in the plane of the chromophore (*cf* Figs. 9 and 10). Equation (6) adapted for the case of aromatic steroids of local C_s symmetry and having one strong substituent becomes:

$$\epsilon(\mathrm{sm})_{\parallel} = \epsilon(\mathrm{sm})\cos^2\bar{\alpha} = \epsilon_i(\mathrm{sm})\cos^2\gamma + \epsilon_{vi}(\mathrm{sm})\cos^2\beta$$
$$+ \epsilon_{vv}(\mathrm{sm})\sin^2\beta$$

$$\epsilon(\mathrm{sm})_{\perp} = \epsilon(\mathrm{sm})\sin^2\bar{\alpha} = \epsilon_i(\mathrm{sm})\sin^2\gamma + \epsilon_{vi}(\mathrm{sm})\sin^2\beta$$
$$+ \epsilon_{vv}(\mathrm{sm})\cos^2\beta, \qquad (14)$$

where β is an angle defined by the normal to the bond axis of the strong substituent and the axis of orientation. It is expected that in general, angles γ and β have similar values. In aromatic steroids with substitution patterns of local C_{2v} symmetry angles γ and β are equal. The induced and vibrational intensities presented in Table 1 have been calculated using eqns (11) for the cases of C_{2v} symmetry, and eqns (14) for the cases of C_s symmetry. $\epsilon_{vi}(\mathrm{sm})$ was estimated, as previously, from the data of TMB and HMB. The experimental data of steroids confirm this assumption. Spectroscopic moments of individual substituents may be determined by the usual vector addition scheme,[1,4] once the resultant $\mathbf{m}_i$ vectors are known. The spectroscopic moments which could be determined from the present LD data are listed in Table 2. One compound, TBCA, could not be given a quantitative treatment, as its weak ^1L_b band is completely masked by the strong red shifted ^1L_a band. In fact, the ^1L_b band does not appear at all in the isotropic spectrum, its position being revealed only by the LD resolved spectrum (Fig. 7).

The ^1L_a system

The LD measurements give the possibility of studying the polarization changes of ^1L_a band on substitution. Because of the strong overlap with the ^1B system, no quantitative evaluation of spectroscopic moments could be achieved. Nevertheless, the theory may be tested on a qualitative basis.

The ^1B system

The intensity of this initial strong band shows little

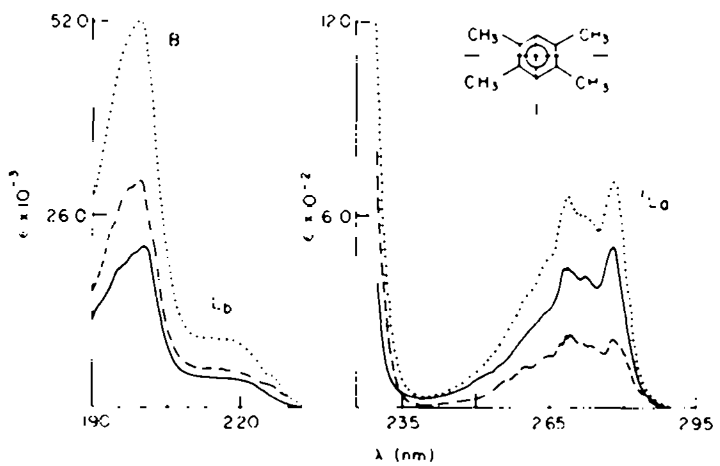

Fig. 8. Resolved spectrum of Durene: (· · · · ·) the isotropic spectrum; (——) the long axis polarized component; (-----) the short axis polarized component.

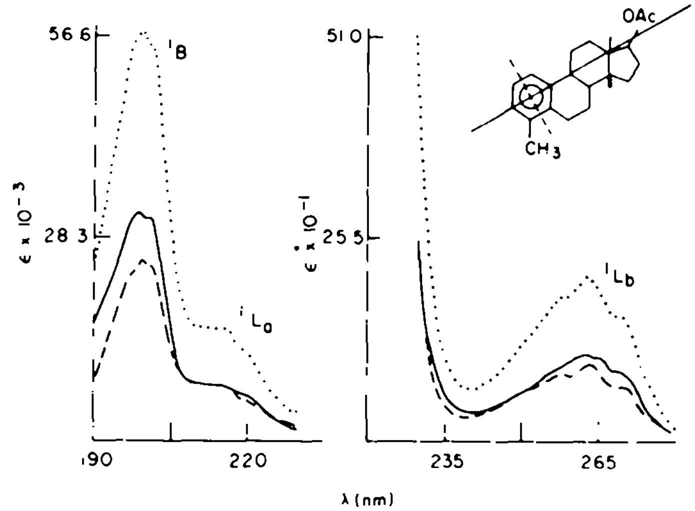

Fig. 9. Resolved spectrum of steroid 1: (· · · · ·) the isotropic spectrum; (——) the component polarized parallel to the axis of orientation; (-----) the component polarized perpendicular to the axis of orientation.

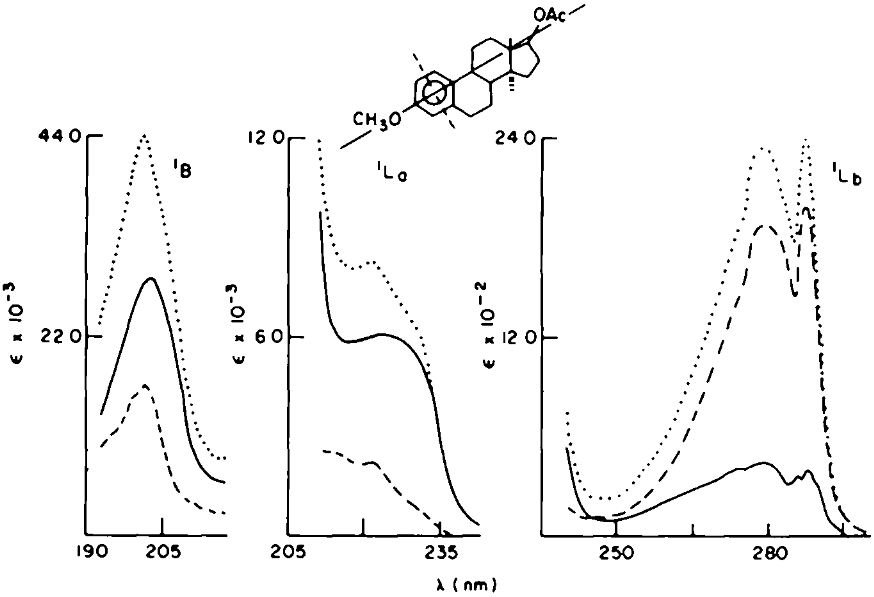

Fig. 10. Resolved spectrum of steroid 4: (· · · · ·) the isotropic spectrum; (——) the component polarized parallel to the axis of orientation; (-----) the component polarized perpendicular to the axis of orientation.

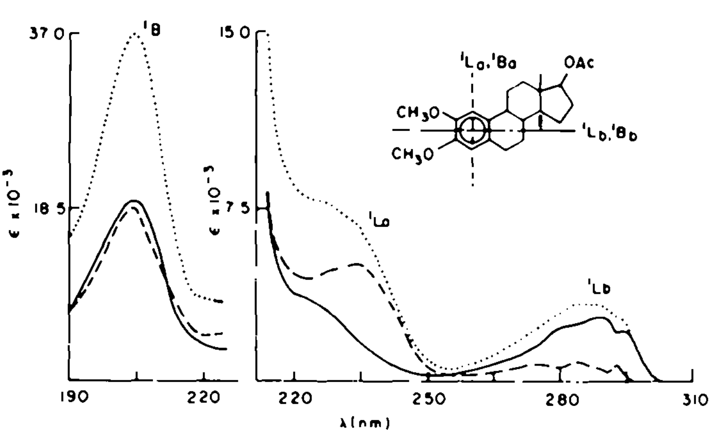

Fig. 11. Resolved spectrum of steroid 6: (· · · · ·) the isotropic spectrum; (——) the component polarized parallel to the local C_2 symmetry axis; (-----) the component polarized perpendicular to the local C_2 symmetry axis.

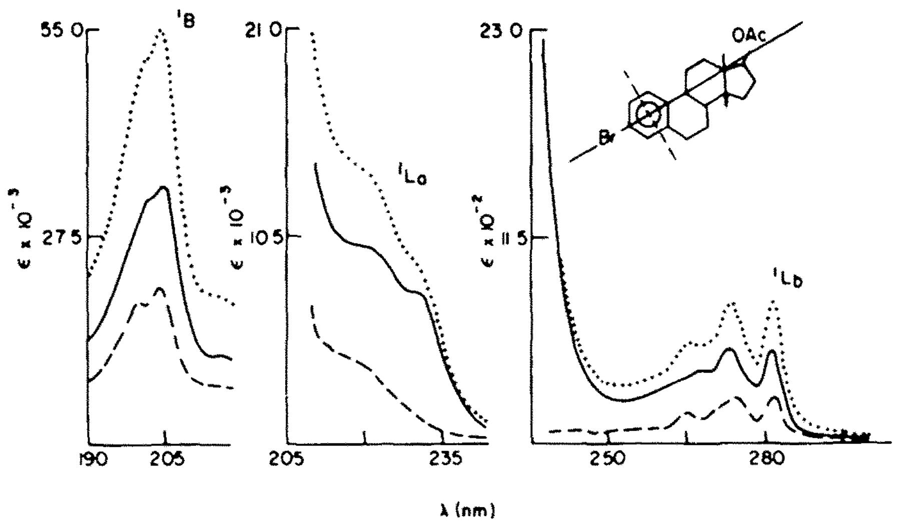

Fig. 12. Resolved spectrum of steroid 8: (· · · ·) the isotropic spectrum; (——) the component polarized parallel to the axis of orientation; (– – – –) the component polarized perpendicular to the axis of orientation.

change, on a relative scale, for different substitution patterns.

It is expected that substitution will affect the ^{1}B system primarily by lowering the symmetry of the chromophore. When the substitution pattern has D_{2h} or C_{2v} symmetry, the ^{1}B band should split into a pair of components, polarized in orthogonal directions.[2] The LD technique offers a very sensitive tool for detecting this effect.

RESULTS AND DISCUSSION

The ^1L_b and ^1L_a systems

The principal new observation that may be made on the basis of the results summarized in Tables 1 and 2 and the resolved UV spectra is that the vibrational intensity of the ^{1}L$_b$ band is by no means constant in all benzene derivatives.[1-4] The vibrational intensity is strongly influenced by the symmetry of the substitution pattern and by the effectiveness of the substituents with respect to the ^{1}L$_a$ transition. There is a very clear correlation between the magnitude of the allowed component of the ^{1}L$_a$ system and the magnitude of the vibrational intensity of the ^{1}L$_b$ system.

The vibrational intensity of the ^{1}L$_b$ system is unequally distributed among vibronic transitions belonging to different symmetry species. Those vibrations which are effective in mixing the ^{1}L$_b$ and ^{1}L$_a$ states produce enhanced vibronic transitions. These vibronic transitions are polarized in the direction of ^{1}L$_a$ transition.

In previous studies based on intensity measurements of isotropic solutions the vibrational contributions were assumed to be isotropic and of about the same values in all types of substituted benzene molecules.[1-4] While this approximation is quite reasonable in cases of weak substituents, theory suggests,[6] and our experimental results confirm, its complete inadequacy for the treatment of substituents producing strong effects. Using the LD-derived vibrational intensities we obtained quite accurate spectroscopic moments which are independent of the kind of substitution pattern even for strong substituents like OMe (Table 2). There is only one exception; the moments obtained from *para*-disubstituted derivatives are systematically lower. Some kind of "saturation effect" may account for this behaviour.[4] In all other cases the variations observed in the moment of a certain substituent in different substitution patterns remain always within the accuracy of the measurements. These observations strongly suggest that previous difficulties, encountered when applying the simple concept of independent spectroscopic moments to strong substitutents, should be primarily ascribed to the improper treatment of the vibrational intensity, rather than to some neglected second order electronic effects.

The influence of substitution on the ^{1}L$_a$ band may be inferred from the resolved absorption spectra. A qualitative agreement with Sklar theory is always observed. Thus, the angles between the directions of polarization of the ^{1}L$_a$ and ^{1}L$_b$ bands are in general close to 90°. The induced component which adds to the initial intensity of the ^{1}L$_a$ transition is in all cases prominent in the 0–0 region of the band.

Table 2.

Subsitutent	Substitution Pattern	Spectroscopic moment (cm m/l)$^{1/2}$
OCH_3	*para*-DMB	+26
	Steroid 4	+33
	Steroid 5	+35
	Steroid 6	+36
CH_3	*para*-xylene	+6
	Durene	+9
	Steroid 1	+8
CH_2–CH– / CH_2–CH_2	Steroid 2	+14
	Steroid 3	+12
Br	Steroid 8	+4
OAc	Steroid 9	+10
$COOCH_3$	*para*-DMTP	−17.5
$N(CH_3)_2$	*para*-TMPD	−21

The effectiveness of a substituent towards the ^1L_b and ^1L_a systems is not always the same. A striking example is bromine, which acts as a weak substituent with respect to ^1L_b system, while it has a strong effect on the ^1L_a system. The charge-transfer character acquired only by the ^1L_a band on substitution[2,6,28] may be responsible for this phenomenon. Unusual strong vibrational components due to such intense ^1L_a bands may appear in the otherwise weak ^1L_b systems in cases of substituents displaying this effect.

Some "anomalies" and apparent exceptions may be now easily rationalized on the basis of our new observations. No "exaltation" of the spectroscopic moments[4] is needed to explain the abnormal high intensity of ^1L_b transition of durene. The enhanced absorptivity is due to the vibrational term, as has alternatively been proposed.[4] The data listed in Tables 1 and 2 show that, due to molecular symmetry, the vibrational component derived from the ^1L_a band is indeed enhanced in this case, while the value of the CH_3 spectroscopic moment remains normal.[29]

The unequal effect of a substituent on the ^1L_b and ^1L_a bands explains the enhancement of the vibrational intensities of steroids 8 and 9 (Table 1). In the case of steroid 8, the vibrational ϵ_{vv}(sm) component, polarized parallel to the C–Br bond axis, is found to be much larger than ϵ_z(sm), which is polarized at 90° with this direction (Table 1). If the vibrational ϵ_{vv}(sm) component, borrowed from the intense ^1L_a band, were not taken into consideration, an induced transition moment polarized along the C–Br band axis should be postulated for the ^1L_b system. Such a result is, of course, incompatible with theory.

Finally, the ^1L_b system of TBCA which, according to theory, should be very weak,[30] does not appear at all in the isotropic spectrum of this compound. The LD spectrum indicates that the ^1L_b system is completely masked by the strong ^1L_a system. In this case, again, the trends manifested by ^1L_b and ^1L_a systems are not identical, ^1L_b becoming very weak, while ^1L_a gains additional intensity and shifts to the red. From theoretical considerations[2,8,28,31] it was shown that a low-lying charge transfer state is expected to interact with the ^1L_a state in benzenes *para*-substituted with donor-acceptor substituent pairs.

The ^1B system

The strong, allowed ^1B system is much less sensitive to substitution than the forbidden ^1L_a and ^1L_b systems. The splitting of ^1B systems into a pair of components with orthogonal polarizations can be observed only in the case of TBCA and DMB. In all other compounds the $d_0(\lambda)$ values over the ^1B band are quite constant and the respective resolved spectra show orthogonal components that are degenerate in energy and are of the same order of magnitude. The large splitting observed in TBCA, with the transversal component shifted to the red (Fig. 7), is characteristic of benzenes *para*-substituted with strong donor-acceptor substituent pairs.[12]

In homo *para*-substituted benzenes no effect, or merely a small effect, is observed, even with very strong substituents. This can be seen in the resolved spectra of TMPD, DMTP and DMB (Figs. 4–6). In DMB the transversal component is slightly blue shifted.

Splitting occurs only when the substitution pattern is *para*. Otherwise, even in the presence of strong substituents, the ^1B system remains two-fold degenerate. This can be seen in the resolved spectra of the aromatic steroids and also from the LD spectra of some benzoates.[12]

The behaviour of ^1B system on substitution suggests that intersubstituent charge transfer states, which interact with the ^1B benzenoid state, may be responsible for the splitting in the *para*-substituted derivatives.

APPLICATIONS OF LD DATA TO THE STUDY OF AROMATIC OPTICAL ACTIVITY

Knowing the directions of electric dipoles involved in certain optically active transitions is often a necessary first condition for the application of circular dichroism (CD) to determinations of absolute configuration in chiral aromatic molecules.

When two or more aromatic chromophores are strongly coupled via dipole–dipole interactions, the chirality of their spatial arrangement may be directly deduced from the CD spectrum only if the coupled electric moment dipoles are known.[11,13,14]

The rationalization of benzenoid ^1L_b and ^1L_a Cotton-effects originating in inherently symmetric chromophores which are only slightly perturbed by their asymmetric molecular environments is less straightforward, but also in this case no satisfactory method of interpretation can be conceived without knowing the directions of the respective electric transition moments.[12,17] As has been already pointed out,[12] estimates of these directions based on spectroscopic moments derived from intensity measurements do not seem to be sufficiently accurate and reliable for the CD studies. Moreover, since the induced and vibrational components of the total transition intensity may lead to completely different Cotton-effects,[33] it is important to have a method of evaluating their relative importance, before attempting an interpretation of the observed CD in terms of one of them. Our linear dichroism method furnishes direct experimental evidence concerned with both the directions of the electric transition moments, and the magnitudes of vibrational components of various substituted benzene chromophores.

To estimate the accuracy of the values reported in Tables 1 and 2, let us analyze the main sources of error expected in measurements and computations. We concentrate on the steroidal compounds which are of direct interest in the CD analysis, but similar conclusions are expected for the other compounds, as well. The observed variations in the measured d_0 values are within a ±3% range.[34] Considering also possible errors in the location of molecular axes of orientation (±2°) and in the f values (±0.01) caused by small geometrical changes in the steroidal skeleton on substitution,[15,16,32] an absolute uncertainty of about ±3° is estimated for the values of angles α and γ. The resulting spectroscopic moments are expected to have a relative accuracy of *ca.* ±7%. However, since further assumptions are involved in the derivation of γ angles from the experimental data, this estimated accuracy is eventually too optimistic. Apparently, the assumed values of β angles in the low-symmetry substitution patterns might constitute sources of additional errors. However, comparing the spectroscopic moments derived from steroids 4 and 5 (low local symmetry, C_s) with that derived from steroid 6 (local symmetry C_{2v}), relative deviations of less than 6% are observed (Table 2). We thus conclude that the approximate nature of some of our assumptions does not seem to lead to deviations beyond the limit of experimental accuracy. The uncertainties in the values of vibrational components depend on the substitution pattern, and range from ±10% in chromophores having relatively large vibrational components and small induced intensity (steroid 1), to values as large as ±40% in cases in which the vibrational contributions are small compared with the large induced intensity (steroid 6).

As will be shown in a following paper,[17] an absolute accuracy of about ±3° for the values of γ angles is satisfactory in most applications of LD data to circular dichroism problems, while only estimates of the orders of magnitude are necessary for the vibrational contributions.

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[18] The dichroic ratio, $d_0(\lambda)(OD_{\parallel}/OD_{\perp})$, is the ratio of optical densities for light polarized parallel and perpendicular to the stretching direction of the polyethylene film.[15,16]

[19] The relations between d_0, f and α are given in the following equations:

$$d_0 = \frac{OD_{\parallel}}{OD_{\perp}} = \frac{f \cdot \cos^2 \alpha + \frac{1}{3}(1-f)}{\frac{1}{2} f \sin^2 \alpha + \frac{1}{3}(1-f)}$$

for elongated and disk-like molecules.[16,20] For planar-shortened molecules two parameters of orientation were shown to be necessary.[16,20] When the transitions are in-plane polarized, one obtains:

$$d_0 = \frac{f' \cdot f'' \cos^2 \alpha + \frac{1}{6}(2 + f'' - 3f' \cdot f'')}{\frac{1}{2} f' \cdot f'' \sin^2 \alpha + \frac{1}{12}(4 - f'' - 3f' \cdot f'')}.$$

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[23] The f's are calculated using the formula of Ref. 19 with the following α values: 0° for TMPD and TBCA, 20° for DMB and 10° for DMTP.

[24] The f's of disk-like molecules calculated with the formula of Ref. 19 are negative numbers when the orientation axes, which are perpendicular on the molecular planes, are preferentially oriented perpendicular to the stretching direction of the film.[16]

[25] The noise level of our measured $d_0(\lambda)$ curve corresponds to about 20 units of ϵ(sm) for the ^1L_b band, and 200 and 1000 units for ^1L_a and ^1B bands, respectively. Nevertheless, the fluctuations are statistically distributed and no systematic deviations from the mean value, indicating an out-of-plane component, can be observed (Fig. 2). Relatively small out-of-plane components were, however, reported to appear in the crystal spectrum of HMB.[8]

[26] It has to be noted that vector addition of vibronic transition moments polarized in orthogonal directions does not occur, as they are derived through vibrations belonging to different symmetry species.[6]

[27] Our LD measurements on TMB and HMB strongly support this assumption.

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[30] The substituents have spectroscopic moments of opposite sign in this case.[3]

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[34] Each LD measurement was repeated on several different film samples using two different methods (the waveplate and the PNP[15]).