Linear Dichroism of [2.2.2.2]Paracyclophanetetraene and [2.2.2.2.2.2]Paracyclophanetetraenediyne in Stretched Polyethylene Film

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Polarized absorption spectra were measured on [2$_4$]paracyclophanetetraene and [2$_6$]paracyclophanetetraenediyne in polyethylene film in the absorption region 220–250 nm. The results are discussed in terms of transition moment directions and deviations of the benzene rings from planarity.

Unsaturated hydrocarbons with cyclic conjugation around the perimeter such as annulenes and bridged annulenes have long been of interest to chemists both from a synthetic and a theoretical point of view.[1-5] The incorporation of benzene rings into the annulenes quench some of the interesting and unusual properties connected with the annulene character even if the benzene rings are bonded in the *ortho* or *para* positions to maintain a cyclic conjugated π-system. The latter type of compounds, paracyclophanes with unsaturated bridges, which are large enough to adopt a fairly planar conformation, have recently become available from multiple Wittig reactions.[6] The neutral compounds show properties typical of normal aromatic derivatives. More interestingly, their dianions behave differently, *e.g.* they sustain large diamagnetic ring currents in strong magnetic fields like the annulenes.[7-11] Simple Hückel calculations, assuming completely planar structures, show a good correlation between the energies of the LUMO's for a series of cyclophanes and the reduction potential for a reversible two electron process.[12] The Hückel approximation thus seems to give a fair description of the delocalization of the two extra electrons over the entire cyclophane. It is interesting to note that the energies of the LUMO's are the same for a series of (2$_n$)paracyclophanes with unsaturated bridges ($n = 2,4,6$...).[13] Less surprisingly, the Hückel orbital energies do not correlate well with UV data. The high symmetry of some of the cyclophanes does in fact complicate the assignment of the electronic transitions. In order to obtain a better understanding of their electronic transitions and photophysical properties, we studied the linear dichroism of two cyclophanes oriented in stretched polyethylene film. The two cyclophanes have identical HOMO and LUMO energies according to Hückel calculations.[13]

Experimental

Compounds *1* and *2* were available from previous work.[14-15] The anisotropic samples were prepared by dissolving the compound in chloroform and then letting the concentrated solution absorb into the polyethylene film. The absorption time was varied from 5 min to several h in order to obtain samples with different concentrations. Polyethylene reference films without solute were prepared in the same manner. The films were washed with ethanol, to remove nonabsorbed crystalline substance from the surface, and dried

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before use. The polarized absorption spectra were recorded on a Cary 219 spectrophotometer equipped with a Glan air-space polarizing prism.

Analysis of dichroic spectra

There are several methods available for evaluating polarized spectra of partially oriented molecules.[16-20] However, those using more than one orientation parameter[16-18] are known to give the most accurate results. We have in this study adopted the method associated with the S_{ii} notation of orientation parameters.[16]

Linear dichroism (LD) is the difference in absorption between linearly polarized light with respect to two fixed coordinate axes Z and Y [eqn. (1)]

$$LD = A_Z - A_Y \tag{1}$$

A useful choice of coordinates in stretched film experiments is to assign the Z-axis along the stretching direction and the Y-axis perpendicular to it (both axes in the plane of the stretched film), as given in eqn. (2)

$$LD = A_\parallel - A_\perp \tag{2}$$

Assuming uniform orientation distribution around the stretching direction, the isotropic absorbance (A_{iso}) can be written as in eqn. (3)

$$A_{iso} = (A_\parallel + 2A_\perp)/3 \tag{3}$$

From equations (2) and (3) it is convenient to calculate a 'reduced linear dichroism' (LD^r), which is independent of path-length and solute concentration[16] [eqn. (4)]

$$LD^r = LD/A_{iso} = 3(A_\parallel - A_\perp)/(A_\parallel + 2A_\perp) \tag{4}$$

A reduced absorption coefficient (A_i^r) is defined [eqn. (5)]

$$A_i^r = A_i/A_{iso}, \quad i = x,y,z \tag{5}$$

where A_{iso} of equation (3) also can be written [eqn. (6)]

$$A_{iso} = (A_x + A_y + A_z)/3 \tag{6}$$

with A_i being the absorption that should be ob-

served when the light is polarized parallel to the molecular symmetry axes i ($i = x,y,z$). Using equation (5) and the orientation parameters S_{ii}, LD^r can be written [eqn. (7)]

$$LD^r = A_x^r S_{xx} + A_y^r S_{yy} + A_z^r S_{zz} \tag{7}$$

By assuming negligible out-of-plane polarized absorption (x-polarization), at least in parts of the spectrum, the orientation parameters S_{yy} and S_{zz} as well as the components A_y and A_z can be evaluated. There are only two independent orientation parameters since [eqn. (8)]

$$S_{xx} + S_{yy} + S_{zz} = 0 \tag{8}$$

In case of overlapping components, the spectrum can still be resolved by a trial-and-error simulation procedure using averaged dichroic ratios and Gaussian absorption curves[21] or by a similar method developed by Thulstrup et al.[17] When S_{yy} and S_{zz} have been determined and the 'two-component' parts of the spectrum resolved, the more complex three-component parts may be investigated.

Results and discussion

The general features of the dichroic and isotropic absorption spectra of the conjugated cyclophanes 1 and 2 are similar. The spectra consist of essentially three parts: i) global transition in the conjugated π-system, ii) local chromophore transitions in the benzene rings and iii) local chromophore or higher order transitions in the substituted ethylene/acetylene moieties and global π-system, respectively.

1

2
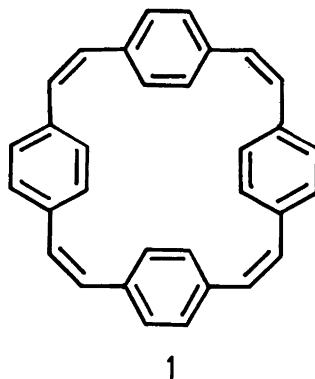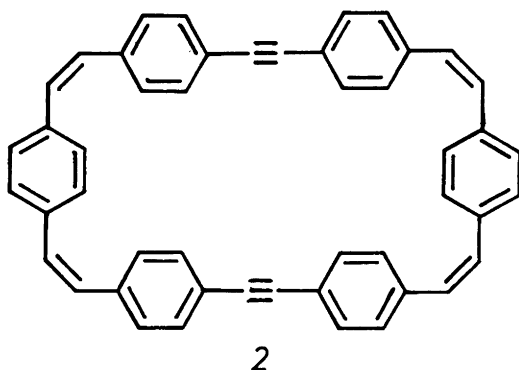
[2₄]Paracyclophanetetraene (1)

The LD^r spectrum of *1* can be resolved in terms of four absorption bands (Fig. 1). Two of them, at 240 nm and 261 nm, most probably originate from local chromophore absorptions of the benzene rings while the other two, at 304 nm and 360 nm, can be ascribed to the global π-system. Inspection of models suggests that the molecule can be considered as belonging to the D_{2d} symmetry group, an assignment supported by the results of molecular mechanics calculations[22] and X-ray studies[23]. In this point group only transitions of B_2

and *E* symmetries are allowed. In order to determine the orientation parameters we need to consider the distribution and symmetry of some of the highest occupied and lowest unoccupied energy levels in the molecule. Molecular orbital calculations of SCF-PPP-CI and CNDO/S type[24] predict the nondegenerate HOMO and LUMO levels to be of A_1 and A_2 symmetry, respectively, while the doubly degenerate NLUMO levels are of *E* symmetry. Thus the band at 304 nm, resulting from the HOMO-NLUMO transition, is allowed and polarized in the molecular plane, *i.e.* yz-polarized. The HOMO-LUMO transition in the molecule is, however, of A_2 symmetry and forbidden. The linear dichroism results may suggest a vibrational coupling of the LUMO – level with vibrations of *E* and B_1 symmetry. This can explain the sudden increase of the dichroic spectrum at 360 nm and the following decrease at longer wavelengths as the result of two different vibrational processes: for instance, if vibrations of *E* symmetry were responsible for the intensity at 360 nm and vibrations of B_1 symmetry for that around 370 nm. It can be noted that vibrations of *E* symmetry would, according to the orientation parameters, produce a larger increase in the dichroic spectrum than other types of vibrations. With these assignments, we get the following ori-

Fig. 1. Isotropic absorbance and reduced dichroism of *1* in polyethylene film. The sum of contributions of the four Gaussian bands (——) is shown by the dashed line.
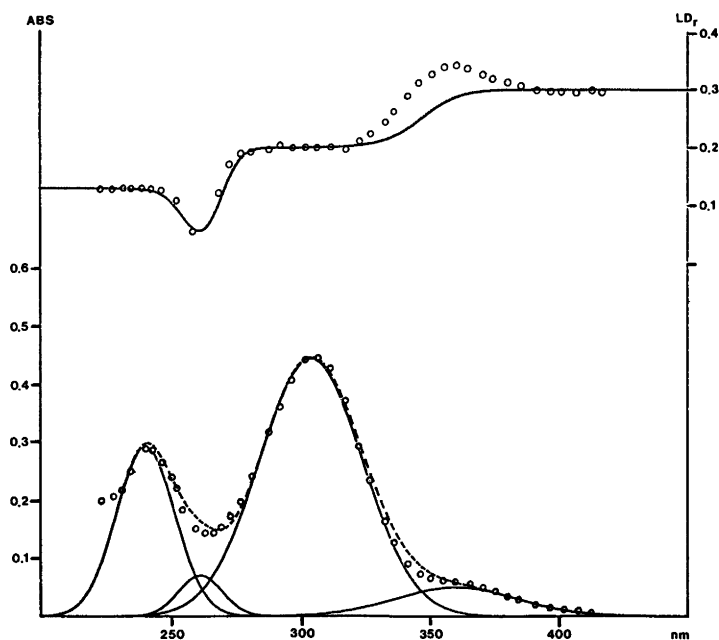
entation parameters for the molecule in the poly-
ethylene matrix:

$$S_{yy} = S_{zz} = \tfrac{1}{3}LD^r (304) = 0.067$$
$$S_{xx} = -S_{yy} - S_{zz} = -0.133$$

Having obtained values of the orientation par-
ameters we turn to the examination of the local
transitions in the molecule, due to the benzene
rings. In benzene itself, the lowest transitions oc-
cur at 255 nm ($^1B_{2u}$) and 200 nm ($^1B_{1u}$ or $^1E_{2g}$).
Having substitution effects in mind, these tran-
sitions can be correlated to the absorptions at 261
nm and 240 nm, respectively. The local decrease
in LD^r at 261 nm can then be accounted for by
out-of-plane transitions[16] from the benzene rings.
Since we know from calculations[22] and X-ray
studies[23] that the four ethylene bridges joining
the rings are practically coplanar, this permits us
to estimate an angle of deviation from planarity
of these rings. Equation (7) can, for this purpose,
be written [eqn. (9)]

$$LD^r = \tfrac{3}{2}\{S_{xx}(\sin^2\alpha_z + \sin^2\alpha_y) + S_{yy}\cos^2\alpha_z + S_{zz}\cos^2\alpha_y\} \qquad (9)$$

where α_z and α_y are defined in Fig. 2. Assuming
$\sin\alpha_z = \sin\alpha_y = \sin\alpha$, an assumption supported
by calculations[22] and symmetry considerations,
equation (9) can, by using equation (8), be writ-
ten into a more convenient form [eqn. (10)]

$$LD^r = \tfrac{3}{2}\{(3<\sin^2\alpha> - 1)S_{xx}\} \qquad (10)$$

where the average allows for the possibility of a
conformational distribution. This gives an 'aver-
age' angle of twist with respect to the bridges of
41.2° which is only slightly larger than the values
obtained from calculations and X-ray studies on
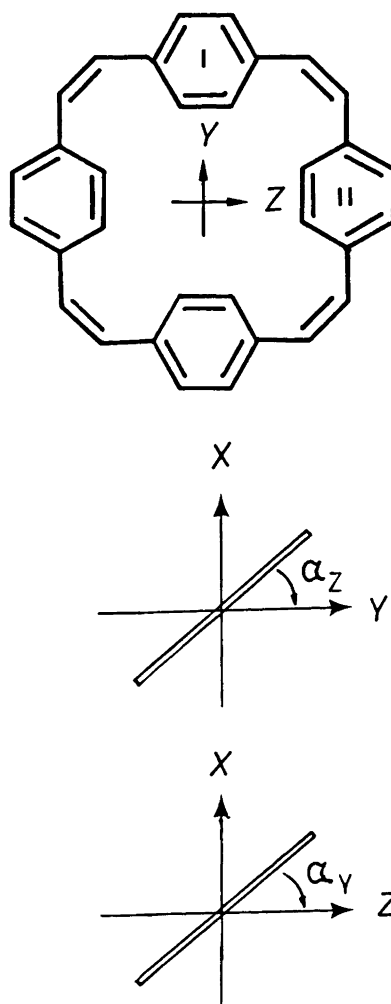crystals (33.4° and ca 35°, respectively).[22-23] On

Fig. 2. Local coordinate system of 1.

the other hand, the corresponding value, ob-
tained by gas electron diffraction, for cis-stilbene
is 43.2 ± 3.2°.[25] For a more detailed discussion of
symmetry and structure, see Liljefors and Wen-
nerström.[22]

[2₆]Paracyclophanetetraenediyne (2)

The LD^r spectrum (Fig. 3) of 2 is more complex
compared to that of 1. One similar feature, how-
ever, is the local benzene ring transition occur-
ring around 240 nm. UV and LD^r spectra indicate
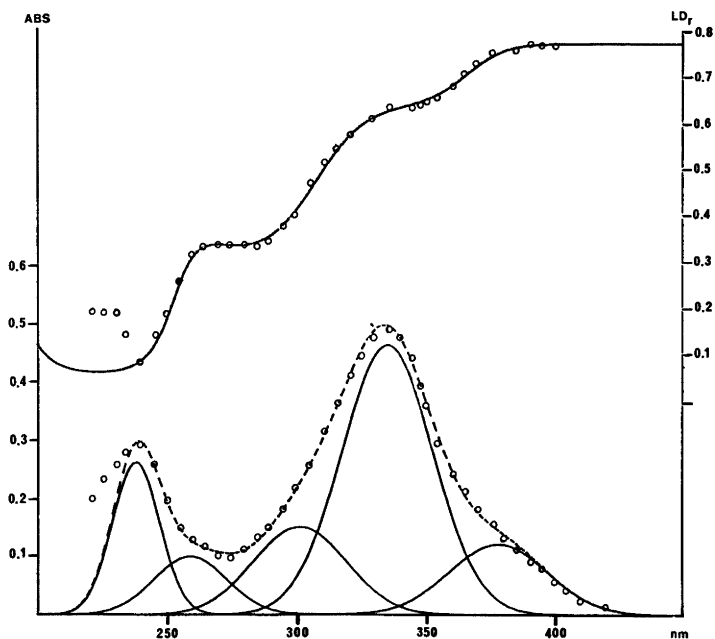two global chromophore transitions at 335 nm

Table 1. Values of LD^r and S_{ii} (i = x,y,z) for some
conjugated cyclophanes.

Com-pound	LD^r		S_{zz}	S_{yy}	S_{xx}
	z polarized	y polarized			
1	0.200 (304)		0.067	0.067	-0.133
2	0.770 (378)	0.630 (335)	0.257	0.210	-0.467

and at 378 nm with y- and z-polarization, respectively. Inspection of the symmetry of the molecular orbitals (PPP-SCF-CI type calculations) supports this assignment indicating, however, the HOMO-LUMO transition to be forbidden and the observed bands to be of higher order, *i.e.* HOMO-NLUMO and HOMO-NNLUMO transitions. Furthermore, two additional bands have to be introduced in the region 250–310 nm in order to resolve the UV and LD^r spectra. These bands might be either local tolan chromophores or, which is more likely, higher transitions. Rewriting equation (7) [eqn. (11)]

$$LD^r = \{(3S_{xx} - 2S_{yy} - S_{zz})<\sin^2\alpha> + (2S_{yy} + S_{zz})\} \qquad (11)$$

assuming $\sin \alpha_z = \sin \alpha_y = \sin \alpha$ (Fig. 4) one can, by using the local chromophore band at 238 nm, calculate the angle of deviation from planarity to 34.2°, which is relatively close to the value of 28.3° predicted by molecular mechanics calculations.[24] This is also a reasonable value when com-
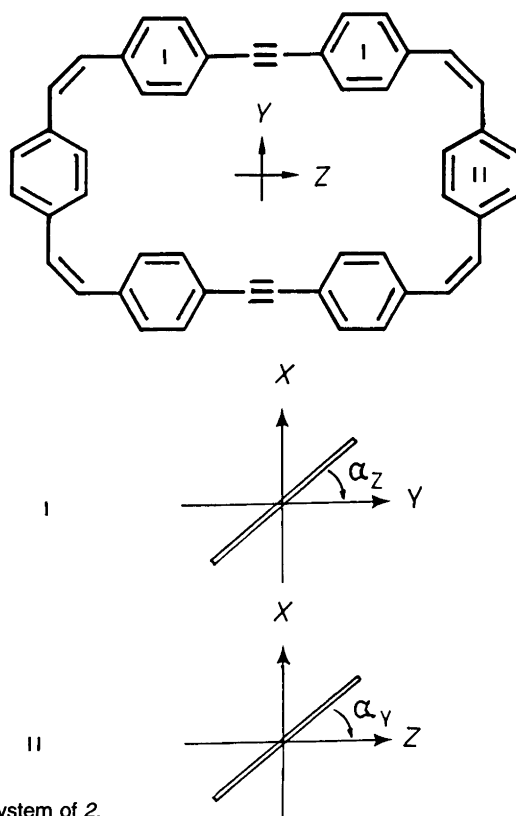

Fig. 4. Local coordinate system of *2*.

pared to that for *1*, since *2* is, according to the calculations, more flexible, thus being able to adjust the double bond bridges better to attain a planar conformation. Note that the band at 240 nm in *1* is shifted to $\simeq205$ nm in *2*. This band was not included in the simulation since it cannot significantly influence the LD^r spectrum at 238 nm.

One characteristic feature of the measured isotropic absorption spectra in the polyethylene matrix is a bathochromic shift compared to the spectra in cyclohexane. These shifts are most easily detected for the intense band of the UV spectrum. In *1*, the smallest and most rigid molecule, this shift is insignificant, while *2* shows a shift of 13 nm. Since the ultraviolet spectrum is very sensitive to conformational changes affecting the conjugated π-system, the shift could indicate a more planar conformation in the polyethylene matrix of the more flexible cyclophane *2*.

Conclusions

Polarized absorption spectroscopy is shown to provide valuable information about the directions of the global transition moments for some conjugated cyclophanes orientated in stretched polyethylene film. From the local transitions in the benzene rings it has also been possible to confirm a rotation of the benzene rings out of the molecular plane. Linear dichroism thus seems to present important possibilities in conformational analysis.

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