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The molecular and electronic structure of dibenzo[g,p]chrysene: A twisted case

Erik W. Thulstrup[1], **Jens Spanget-Larsen**[1], **Jacek Waluk**[2]
[1] Inst. I, Roskilde University, P.O.B. 260, DK-4000 Roskilde, Denmark
[2] Inst. of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Summary. Studies of the electronic structure and spectrum of dibenzo [g,p]chrysene, carried out in 1965 and 1985, were not fully conclusive. They are repeated here by means of improved linear dichroism spectroscopy, quantum mechanical calculations of the spectra, and structural studies. Based on the new evidence, especially the observed transition moment directions, it is concluded that the molecule is nonplanar with D_2 symmetry. The experimentally determined transition moment directions also allow a complete assignment of all significant transitions in the region 25 000 to 45 000 cm^{-1}. All three possible (perpendicular) transition moment directions are represented among the observed electronic transitions.

Key words: Transition moments – Linear dichroism – Dibenzo[g,p]chrysene, conformation and UV spectra of

Introduction

In 1964, the solution UV spectrum of dibenzo[g,p]chrysene (DBC) was published [1] and only a year later, in 1965, the linear dichroism (LD) spectrum of DBC aligned in stretched polyethylene was presented at a conference [2] by a group from Aarhus University, which during this conference for the first time approached Jan Linderberg concerning his possible employment.

The results presented at the 1965 conference were not published further at the time because of problems with the interpretation of the LD spectrum. It was assumed then that all significant intensity was due to π–π^* transitions and that two perpendicular transition moment directions in the molecule (here x and y) would dominate. Furthermore, it was expected that the two axes, x and y, would have comparable, but still distinct alignments in the uniaxially stretched polymer. The spectra [2] showed contributions from two different transition moment directions, but the alignment of these with the sample axis were very different (one well aligned, another poorly aligned). Based on the experience that molecular shape is

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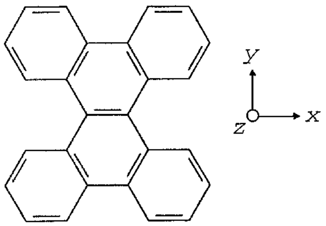
* Dedicated to Jan Linderberg on the occasion of his 60th birthday

the determining factor for the alignment of nonpolar molecules in stretched polyethylene, the observed bands could not be safely assigned to x- and y-polarized transitions.



Twenty years later, in 1985, the main problem was solved [3]. With a more detailed mathematical description of molecular alignment in stretched polymers [4, 5] and supported by new UV LD spectra obtained in stretched polyethylene, magnetic circular dichroism (MCD) spectra, and theoretical studies of the electronic transitions by INDO/S, it was concluded that the transitions along x and y appeared with an almost equivalent alignment in the polymer and therefore were very hard to separate.

The new LD spectra were in complete agreement with those recorded in 1965 [2]. However, it was now clear that the poorly aligned transition moment direction was the "out-of-plane" direction z. The considerable intensity gained by the latter was explained as a result of a distortion from planarity of DBC due to hydrogen crowding in the bay areas. This will make "out-of-plane π–π^*" intensity allowed.

Partly because of a low solute concentration in the sample used in 1985, it was not possible to distinguish clearly between transitions corresponding to the directions x and y [3]. Therefore, the assignments made were primarily based on energy, intensity, and MCD results and were rather tentative. Early this year, new measurements on a better sample, together with new calculations of both molecular conformation and spectra have now made it possible to perform both a more complete assignment of all observed transitions and to draw some conclusions concerning the ground state conformation of DBC.

Experimental and theoretical methods

The use of LD spectroscopy of samples aligned in stretched polyethylene for spectral assignments and evaluations of theoretical models goes back around 30 years. Partly due to valuable support and encouragement from Jan Linderberg, the first results, demonstrating the superiority of the method to most other methods used for transition moment studies, were published in 1968 [6], followed by publication of a more detailed analysis two years later [7, 8].

The experimental efforts are in principle simple: Two spectra are recorded with linearly polarized light on a uniaxially aligned sample, one with the electric vector parallel to, the other with the electric vector perpendicular to the sample axis Z. A stretched polymer (e.g. polyethylene) is a convenient solvent, producing uniaxial samples of solute molecules such as DBC, with the stretching direction as the unique axis Z. For a given transition i, the directional quantitites that may be observed are the squares of the cosines between the transition moment for the transition, $\boldsymbol{M}_i$, and the electric vector $\mathcal{E}$ of the light, averaged over the sample molecules. The two spectra become [4, 5, 7, 8]:

(1) for $\mathcal{E}$ along Z:

$$E_Z = \sum\langle\cos^2(\boldsymbol{M}_i, Z)\rangle A_i = \sum K_i A_i \tag{1}$$

(2) for $\mathcal{E}$ along laboratory axis Y, perpendicular to Z:

$$E_Y = \tfrac{1}{2}\sum(1 - \langle\cos^2(\boldsymbol{M}_i, Z)\rangle)A_i = \tfrac{1}{2}\sum(1 - K_i)A_i, \tag{2}$$

where the sums are over transitions i and A_i is three times the contribution of transition i to the absorbance of an isotropic sample (all K_i in an isotropic sample are $\frac{1}{3}$). This makes it possible to determine K_i for each transition, either directly (for nonoverlapping transitions) or by a trial and error method, called the TEM method [4, 5]. In this method, linear combinations of the two observed spectra are plotted; if a spectral feature disappears from the linear combination $E_z - c_i E_y$, then, according to Eqs. (1) and (2), $K_i = c_i/(2 + c_i)$. K_i measures how well $\boldsymbol{M}_i$ on the average is lined up with the sample axis Z; for alignment of nonpolar molecules in stretched polyethylene this mainly depends on the molecular shape.

For molecules of C_{2v}, D_{2h}, and D_2 symmetry (here labelled "symmetrical" cases) only three different transition moment directions are possible, along the molecular axes x, y, and z. Thus also only three different K_i's may be observed. They are not independent, but add up to one, by definition:

$$K_x + K_y + K_z = 1\,.$$

While it is possible to determine any number of different K-values from the two observed spectra, the very useful separation of the observed intensity into contributions from different transition moment directions, which has been demonstrated for numerous π-electron systems [4–7], is only possible when all intensity in a region is due to only two different K-values. This is the case for planar "symmetrical" aromatic hydrocarbons without out-of-plane polarized intensity or for "rod"-shaped or "disk"-shaped molecules [4, 5]. In the present case, the new spectra reveal three different K's, K_x, K_y, and K_z, as expected in nonplanar "symmetrical" cases. The two observed spectra make it possible to remove intensity corresponding to any one (but not two) of the three K's from the observed spectra which are mixtures of contributions from all three transition moment directions.

Semiempirical calculations [9, 10] have often at low computational costs provided valuable information on both molecular geometry and excitations, with improved spectral assignments as a result. In return, spectroscopic information, including information on transition moment directions from LD spectroscopy, has often provided valuable material for tests and improvements of such theoretical models.

In the present case, ground state geometries were calculated using the MMX force field (PC MODEL) [11]. This led to two different conformers, one of D_2 symmetry, the other of C_{2h} symmetry, as illustrated in Fig. 1. The total ground state energy was almost 5 kcal mol^{-1} lower for the former than for the latter. For comparison with the spectra, INDO/S [12, 13] calculations of electronic transition energies, intensities, and moment directions (excited state symmetries) were performed for both conformers, using the 200 lowest singly excited configurations in the configuration interaction treatment.

Results

The calculated geometries for both the D_2 and C_{2h} conformers are illustrated in Fig. 1, both seen from two different angles. In the case of D_2, the axes are determined by symmetry. In the case of C_{2h}, x is taken as the symmetry axis; the choice of y and z is then arbitrary. We have chosen y pointing horizontally left in the plane formed by the six "central" carbon atoms and z pointing vertically upwards in Fig. 1 (bottom, right). Based on molecular shape, we assume that these axes are the orientation axes [4, 5] for a possible C_{2h} shaped DBC, i.e. that, for example, K_z is equal to the lowest K-value.

Figure 2 shows the two observed UV LD spectra. From the peaks and shoulders in the spectra, only three different K-values could be determined. This was done using the TEM method because of the strong spectral overlap. The set of curves corresponding to the resulting linear combinations of the observed spectra is shown in Fig. 3.

The three K-values resulting from the TEM procedure are:

$$K_x = 0.39 \pm 0.005;$$

$$K_y = 0.367 \pm 0.003;$$

$$K_z = 0.24 \pm 0.01.$$

K_y is determined most accurately due to the very strong and sharp peak near 33000 cm^{-1}. The weak first transition has the same K-value. K_x is best determined from the strong transition near 29000 cm^{-1}, but the very strong peak around

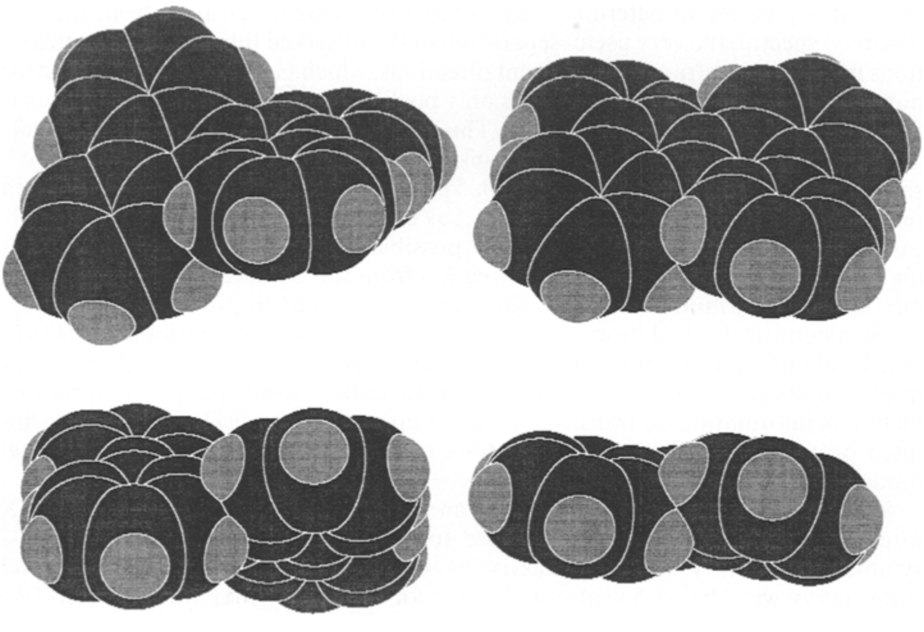


Fig. 1. Calculated ground state conformations of DBC seen from two different angles. Left (*top and bottom*) the D_2 conformer which is calculated to have an energy almost 5 kcal mol^{-1} lower than the C_{2h} conformer shown at right (*top and bottom*)

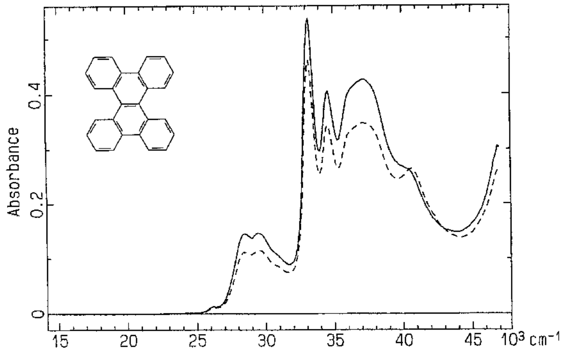


Fig. 2. Observed LD spectra of DBC. Full curve: E_Z, the absorbance recorded with the sample axis z parallel to the electric vector of the light, $\mathscr{E}$. Broken curve: E_Y, the absorbance recorded with z perpendicular to $\mathscr{E}$.

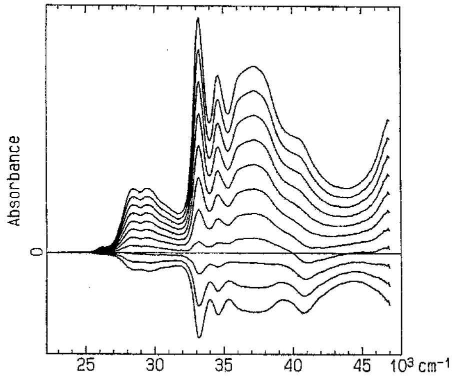


Fig. 3. The TEM procedure [4, 5]. The curves shown correspond to $(1 - K)E_Z - 2KE_Y$, with $K = 0.00, 0.05, \ldots . 0.50$. The K-value of a spectral feature i will be equal to K_i if the feature disappears for $K = K_i$

37000 cm^{-1} seems to have the same K-value. Finally, K_z is determined from the small peak near 41000 cm^{-1}.

The three K-values add up to 0.997, close to the theoretical value of 1.000. For simplicity, labelling of the axes has already now been made in accordance with the assignment resulting from the study.

Equations (1) and (2) can now be rewritten:

$$E_Z = 0.39A_x + 0.367A_y + 0.24A_z, \tag{3}$$

$$E_Y = 0.305A_x + 0.317A_y + 0.38A_z, \tag{4}$$

where A_u, $u = x, y$, or z, is the sum of all contributions to the absorbance due to u-polarized transitions. From these expressions, three linear combinations of the observed spectra are produced, as shown in Fig. 4. In the first combination (top curve), the contributions from z-polarized transitions have been removed. Since K_x and K_y differ slightly, this results in a mix of x- and y-polarized intensity which is only approximately even: $A_y + 1.18A_x$.

In the second linear combination, x-polarized contributions have been removed. Because of the closeness of K_x and K_y, complete removal of A_x introduces A_z with a much larger weight than A_y: $A_y + 7.14A_z$. In the third linear combination, where A_y is removed, A_z appears with a large negative coefficient: $A_x - 6.05A_z$. These two latter curves illuminate the composition of the former curve; the weak absorption around 26000 cm^{-1} as well as the sharp, strong peaks

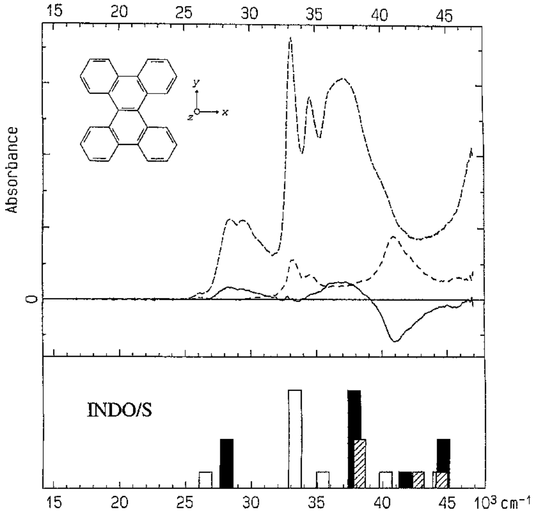


Fig. 4. *Top*: Linear combinations of the observed spectra, each corresponding to only two different K-values (transition moment directions). The broken curve on top corresponds to $6(A_y + 1.18A_x)$, the two bottom curves correspond to $A_y + 7.14A_z$ (broken curve) and $A_x - 6.05A_z$ (full curve).
Bottom: Calculated results for the D_2 conformer. Black bars represent x-polarized transitions, white bars y-polarized transitions, and hatched bars z-polarized transitions. The calculated oscillator strengths are indicated by the height of the bars ($f > 1$, $1 > f > 0.1$, or $0.1 > f > 0.01$)

starting at 33300 cm^{-1} are y-polarized, the less distinct peaks starting around 29000 cm^{-1} and 37000 cm^{-1} are x-polarized.

The "out-of-plane" absorption is easy to recognize, less because of its absence from the first curve, but mainly because of the mirror image effect demonstrated in the two latter curves. This is caused by the prominent appearance of A_z with different signs in the two curves.

The earlier assumed presence of a weaker, z-polarized peak near 33000 cm^{-1} [2, 3] now seems to be triggered by an artifact due to incomplete removal of the sharp y-polarized peak at 33300 cm^{-1} in the curve assumed to represent A_z. The incomplete removal was a result of the assumed common K-value for the x and y directions, which was higher than the actual K-value for this peak. However, the weak peaks at 45500 cm^{-1} in the two latter curves in Fig. 4, which also show a "mirror image" relation, may be an indication of a second z-polarized transition with a K-value around 0.2–0.3.

The agreement between these observations and the calculated results for the D_2 conformation is excellent (Table 1). The calculations predict a weak first transition along y around 26500 cm^{-1} (L_b), followed by a strong, x-polarized (HOMO-LUMO, L_a) transition around 28000 cm^{-1}. In addition to some calculated forbidden or very weak transitions in the region between 30000 and 45000 cm^{-1}, this region is predicted to contain a very strong y-polarized transition at 33300 cm^{-1} (B_b) and an equally strong x-polarized transition around 38000 cm^{-1} (B_a).

The first z-polarized transitions are predicted to be well below 40000 cm^{-1}, but are so weak that they can hardly be observed because of overlap with other, stronger transitions. A medium-strong, z-polarized transition is predicted at 38200 cm^{-1} in poorer, but still acceptable agreement with the observation of a z-polarized peak at 40700 cm^{-1}. A second z-polarized transition, somewhat weaker, is predicted near 42700 cm^{-1}; it corresponds roughly to the second "mirror image" relation, at 45500 cm^{-1}, observed in the two curves containing A_z (Fig. 4).

The fact that both calculated, z-polarized transitions have slightly too low energies, in poorer agreement with experiment than those of the other calculated transitions, may be a result of a less satisfactory determination of contributions

Table 1. Observed and calculated electronic transitions for dibenzo[g,p]chrysene (DBC). Observed wavenumbers $\tilde{\nu}_{max}$ (10^3 cm^{-1}) and ε_{max} (L mol^{-1} cm^{-1}) in *n*-hexane [3], and orientation factors *K* in stretched polyethylene. Calculated $S_0 \rightarrow S_n$ transitions for the D_2 and C_{2h} conformers: Wavenumbers $\tilde{\nu}$ (10^3 cm^{-1}), oscillator strengths *f*, polarization directions, and excited state symmetries

n	Observed			INDO/S (D_2)				INDO/S (C_{2h})[a]			
	$\tilde{\nu}_{max}$	ε_{max}	*K*	$\tilde{\nu}$	*f*	Pol.	Sym.	$\tilde{\nu}$	*f*	Pol.	Sym.
1	26.3	1000	0.37	26.5	0.09	*y*	B_2 (L_b)	26.5	0.02	+ 6°	B_u (L_b)
2	28.7	14000	0.39	28.1	0.33	*x*	B_3 (L_a)	29.2	0.21	*x*	A_u (L_a)
3				29.7	—	—	A	29.4	—	—	A_g
4	33.3	80000	0.367	33.3	1.13	*y*	B_2 (B_b)	33.5	1.33	+ 6°	B_u (B_b)
5				35.1	0.005	*z*	B_1	34.3	—	—	B_g
6				35.3	0.009	*z*	B_1	34.6	0.03	*x*	A_u
7				35.4	0.08	*y*	B_2	35.8	—	—	B_g
8				35.5	0.002	*x*	B_3	36.7	0.14	+ 29°	B_u
9				37.6	—	—	A	37.1	2.08	*x*	A_u (B_a)
10	37.3	70000	0.39	37.8	1.64	*x*	B_3 (B_a)	37.3	—	—	B_g
11	40.7	8000	0.24	38.2	0.27	*z*	B_1	37.8	—	—	A_g
12				39.9	—	—	A	39.8	—	—	A_g
13				40.2	0.04	*y*	B_2	40.6	0.06	+ 51°	B_u
14				41.0	0.002	*y*	B_2	41.5	—	—	A_g
15				41.6	—	—	A	42.2	—	—	B_g
16				41.7	0.03	*x*	B_3	42.7	—	—	B_g
17	45.5[b]		0.2?	42.7	0.06	*z*	B_1	42.8	0.15	*x*	A_u
18				44.3	0.03	*y*	B_2	43.2	—	—	B_g
19				44.5	0.07	*z*	B_1	44.2	0.10	− 12°	B_u
20				44.6	0.28	*x*	B_3	44.4	—	—	B_g

[a] Polarization directions perpendicular to the *x*-axis are given by the angle $\alpha = \sphericalangle(y \rightarrow z)$, see text

[b] Feature observed only in stretched polyethylene

involving σ-orbitals, which are important for z-polarized transitions. In INDO/S calculations on aza-aromatics, for example, it is usually observed that n–π^* transitions are calculated at too low energies relative to π–π^* transitions. It is worth noticing that for the corresponding two z-polarized transitions, calculated for the C_{2h} conformer, the agreement with experiment is even worse.

Otherwise, the agreement between the observed spectra and the calculated transition energies for the C_{2h} conformer is as good as for the D_2 calculations. In C_{2h}, any transition moment direction perpendicular to the symmetry axis is possible; the fact that only three different K-values are observed and that they add up to one, is clearly less consistent with C_{2h} than with D_2, C_{2v}, and D_{2h} for which such a behaviour is expected. A C_{2v} symmetrical conformation can readily be excluded, while a D_{2h} conformation, corresponding to a planar structure, must be excluded, since it is unlikely to provide the observed "out-of-plane" intensity. From this evidence alone, we are led to a tentative conclusion that the symmetry must be D_2.

Further support for this conclusion may be obtained from a more quantitative study of the "out-of-plane" polarized transitions. Changing a planar conformation into C_{2h} with x as the symmetry axis would mix y- and z-polarized intensity and would thus be expected to give rise to K-values between K_z and K_y (between 0.24 and 0.37) for at least some of the formerly y- and z-polarized transitions. This would especially affect the weaker, formerly "out-of-plane" polarized transitions, for which mixing with the stronger transitions would turn moments the most. The expectations are confirmed by the calculated results; formerly y-polarized transitions essentially remain y-polarized, while those calculated transitions that might be assigned to the 40 700 and 45 500 cm^{-1} peaks are predicted to form angles with the y-axis around 30–50°. This would correspond to K-values near 0.3 [4, 5], well above the observed, well determined value of 0.24 for the 40 700 cm^{-1} peak, which lends further support to the D_2 conformation. It must be added that attempts to record an infrared LD spectrum of DBC in stretched polyethylene were not successful; such measurements would most likely have provided an abundance of information on the conformation because of the large number of vibrational transitions available.

The present results are consistent with those of Palewska et al. [14], who found two conformers in Shpolskii matrices at 4.2 K, but with one at an order of magnitude higher concentration. They expect the latter to be of D_2 symmetry. In our spectra only one conformer is observed in the stretched polyethylene, but, due to spectral overlap, we cannot exclude the presence of a small concentration of another conformer with similar transition energies.

LD spectroscopy is regularly used for determination of structures in molecular associations such as dyes or metal ions bound to DNA [4, 5]. The present investigation demonstrates the potential of LD spectroscopy, together with theoretical studies, as a tool for structure determination of individual molecules. So far, such applications have been fairly rare, but the simplicity of both the spectroscopic work involved and of the information provided by transition moment directions seems to make it worthwhile to test the applicability of the method further.

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