THEORETICAL ANALYSIS OF UV, CD AND ORD SPECTRA OF TWO 1,1′-BIANTHRYL DERIVATIVES*

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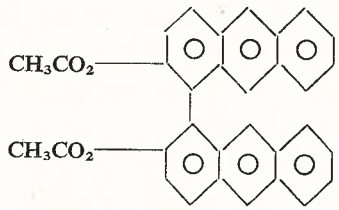
Ultraviolet (UV), circular dichroism (CD) and optical rotatory dispersion (ORD) vibronic spectra of two 1, 1′-bianthryl derivatives are analysed in terms of the theory of vibronic coupling in dimers. Good agreement between theory and experiment is obtained in vibronic structure for all these spectra. This analysis suggests the relative orientation of two anthracene rings in these compounds.

1. Introduction

1, 1′-bianthryl derivatives have a fairly strong optical activity, forming typical examples of intrinsically dissymmetric chromofores.

The electronic dipole transition moments to several electronically excited states do not vanish which is very convenient for theoretical considerations, as one can assume the Condon approximation for electrical and magnetic moments, neglecting their dependence on nuclear coordinates [1]. The compounds, we are interested in, were obtained several years ago by Badger, Jeffers and Kimber [2]. These are



(−) dimethyl-1, 1′-bianthryl-2, 2′-dicarboxylate (DMBADC)

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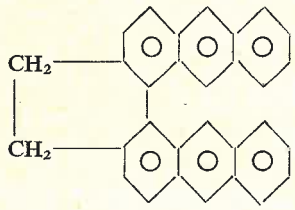

(−) 9,10-dihydrodinaphto (2′, 3′-3,4 : 2″, 3″-5,6) phenanthrene (DHDNP).

The vibronic absorption spectra (UV), circular dichroism (CD), and optical rotatory dispersion (ORD) of these compounds were investigated [3, 4]. In the available frequency range for spectrometer measurements there are four electronic states. Two of them arise from the split B_{2u} anthracene state, and lie in the vicinity of 27000 cm^{-1}, whereas the other two arise from the split B_{3u} anthracene state and have energy close to 39000 cm^{-1} [5]. We will call the two lower states *p*-states, and the two upper ones β-states, according to Clar's classification [6].

It has been established with the help of oriented organic synthesis, that both these compounds have *R*-configuration, in which two anthracene rings form a segment of a right helix [3, 7]. This conclusion was later confirmed by CD measurements of the β-band [4]. In all types of spectra, that have been investigated, one can see quite clear vibronic structures, very well developed in the *p*-band.

The aim of this paper is the interpretation of these structures, and their connection with conformation of the investigated molecules.

We will treat 1, 1′-bianthryl derivatives DMBADC and DHDNP as dimres formed by two anthracene chromofores, and will adopt the vibronic coupling theory in dimers. This theory has been formulated by Witkowski and Moffitt [8, 8a] and developed by Fulton and Gouterman [9, 10]. It was successfully applied to the interpretation of absorption and fluorescence spectra of several dimers [11–15], although in certain cases some refinements were necessary [13, 15, 16].

Weigang [17] has shown how to apply the model formulated in [10] to the calculation of vibronic structure of circular dichroism of a dimer. However, his calculations have not been previously compared with experiment. One can expect that, similarly as in the case of UV spectra, the anthracene dimers will serve as good objects for this purpose. We will calculate the theoretical CD and ORD spectra together with UV spectra to check the consistency of the theory and compare then with the experimental ones. We will see that the conformation of the dimers has a huge effect on vibronic structures of these spectra.

Section 2 is devoted to the theoretical reconstruction of the UV spectra. This gives us a set of parameters for the theory that will be used for calculating the CD and ORD spectra.

Section 3 deals with the interpretation of vibronic structure of CD and ORD.

In Section 4 we discuss some other possible explanations of the observed effects in the spectra.

2. *Absorption spectra*

As we already noted, 1, 1′-bianthryls can be treated as dimers, if one is interested in optical properties of low excited electronic states. The electronic excitation of an anthracene ring is then shared by two chromofores owing to the resonance interaction.

The anthracene dimers were carefully investigated from the experimental and theoretical points of view, with respect to their UV spectra [11, 14, 15]. It is known that the most prominent Franck–Condon progression in the absorption spectrum of an anthracene molecule is formed by C–C stretching vibration with a frequency of 1400 cm^{-1}. This progression can be easily recognized in the absorption to the B_{2u} state and to the B_{3u} state [11, 18].

It was shown, that for not to highly resolved spectra, one can neglect the role other modes play in the vibronic structure of an anthracene UV spectra [11]. We will adopt the same simplification in the interpretation of 1, 1′-bianthryl derivatives spectra.

The model of a dimer with only one spectroscopically active mode is presented in [8a, 10]. Every monomer electronic state becomes split in a dimer, forming two vibronic manifolds of different dipole transition polarization. These manifolds, we will call "plus" and "minus". They have the transition moments $\vec{M}_1+\vec{M}_2$ and $\vec{M}_1-\vec{M}_2$, respectively, where $\vec{M}_1$ is a transition moment of the i-th monomer. The centers of gravity of absorption spectra to these two manifolds are separated by $2|\varepsilon|$, where ε is the parameter that measures the resonance interaction between chromofores. The halfwidth of these spectra is equal to $|\lambda|$, where λ is a displacement parameter of an optically active, totally symmetric mode of a monomer. For the unpolarized absorption spectrum of a dimer, its center of gravity is shifted by $\varepsilon \cos \alpha$ with respect to that of a monomer, where α is an angle formed by $\vec{M}_1$ and $\vec{M}_2$ transition moments.

We have performed the calculations of absorption spectra according to the model presented in [10]. All parameters needed for these calculation were obtained from experimental data.

We got the λ parameter for the β-band from the halfwidth of the absorption band of the anthracene B_{3u} state [11]. Its value is 0.4. We took anthracene, not its derivatives, for this purpose because of the lack of the spectra for the others. Anyway, the vibronic structure in the β-band is so smeared out that knowledge of the exact value of λ for this band is not necessary. The parameter λ for the p-band is somewhat larger then that in the anthracene and reads 1.3 for DMBADC and 1.2 in DHDNP (compare with 1.0–1.1 in anthracene). This larger value of λ can be connected with the interaction between the π-electron system and a substituent, which leads to a redistribution of an electronic cloud after excitation and to a bigger change in C–C distances. It can also result from the fact that we neglect the possibility of a frequency change in the excited state of a monomer.

The transition to the B_{3u} state in anthracene is polarized along the long axis of a molecule, therefore an angle formed by the long axis of two anthracene rings is the same as that formed by electronic transition dipole moments to the B_{3u} state. This angle can be obtained from the measurement of the ratio of the total absorption intensities to plus and minus systems. This ratio reads $(1+\cos\alpha)/(1-\cos\alpha)$, and gives the values of α 95° in

DMBADC and 66° in DHDNP. Compare it with values estimated in a different way by Grinter and Mason [4]. That read 110° and 70°, respectively.

The ε parameters can be, in principle, obtained from the difference in centers of gravity of the plus and minus systems. They were estimated to be 0.7 in DMBADC and 1.2 in DHDNP for the β band, and 0.4 in DMBADC and 1.3 in DHDNP for the p-band.

The estimation of ε for the p-band is connected with some difficulties. This band arises from the B_{2u} state of an anthracene molecule and has polarization along the short ring axis. Had these axes been parallel, only transitions to the minus system were allowed.

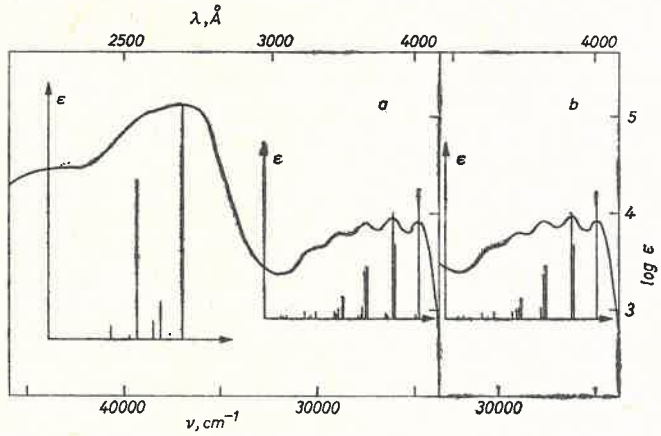

Fig. 1a. Experimental and theoretical absorption spectra of DMBADC. The experimental intensity is given in a logarithmic scale, whereas the theoretical intensities are given in a linear scale. The angle δ was taken to be 10°; b. the p-band and its theoretical reconstruction for $\delta = 0$

The absorption spectrum should then consist of one slightly shorter vibronic progression shifted towards lower energies with respect to that of an anthracene molecule.

Looking at the experimental data of Fig. 1 one sees that this is really the case for DMBADC. However, for DHDNP (Fig. 2) we see, that the progression is long and has a

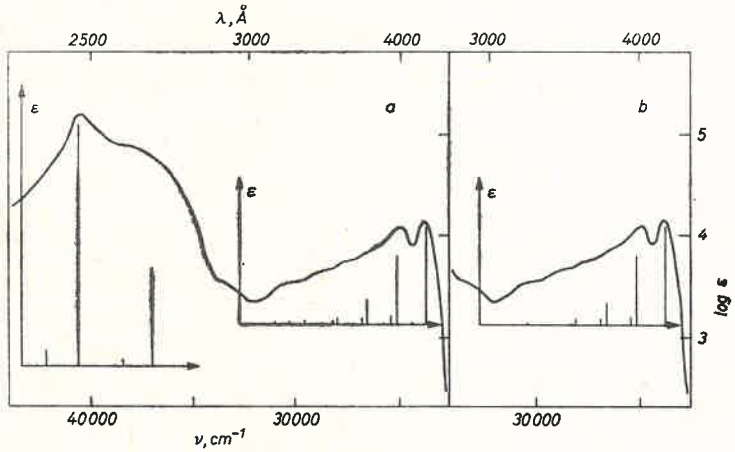

Fig. 2. The same plot as Fig. 1 but for DHDNP

rather high intensity on the high energy side. This leads to a suspicion, that the plus component in the absorption spectrum is not totally forbidden. The most natural reason for this can be the fact that the short axes of two anthracene rings are not parallel forming a 2δ angle. Such hypothetical orientation of the anthracene rings is shown in Fig. 3.

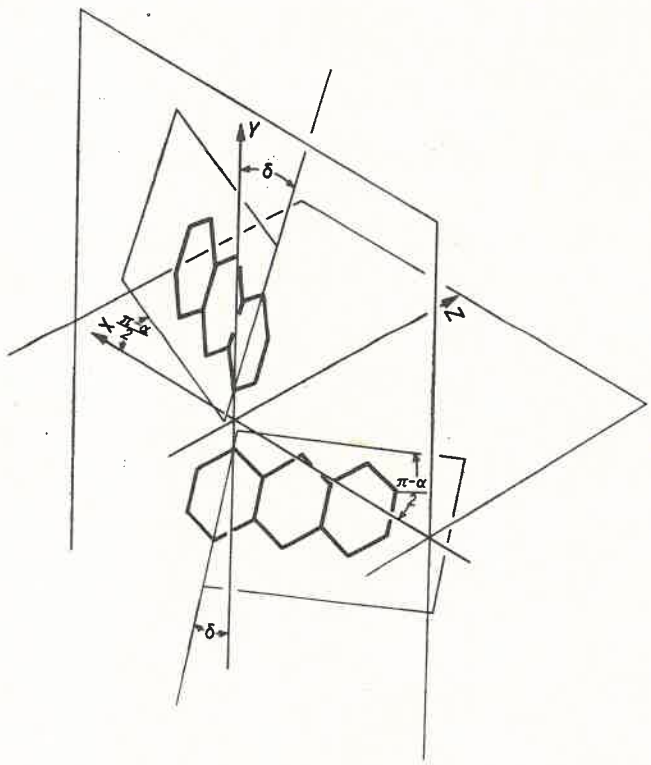

Fig. 3. The proposed arrangement of the two anthracene rings in 1,1′-bianthyl derivatives

As is shown in the Appendix, both polarizations are then allowed in the *p*-band. Also, the plus system becomes active in circular dichroism giving signs of the effect in agreement with experiment. We estimated that δ is close to 10°. This deviation of short axes from the *y*-axis is very probable if one takes into account strains that can arise upon joining rings with an ethylene bridge connected in positions 1, 1′. One should expect a similar structure in DMBADC. Here, the deviations can be caused by repulsion between carbonyl groups of substitutents. However, this deviation in DMBADC is not detectable spectroscopically because the ε parameter for *p*-band is small here, giving a very slight separation of the plus and minus systems, and the resulting spectra are not very sensitive to not too large changes in δ angle. However, even these minimal changes as those seen in Figs 1a, 1b (UV) and Figs 4a, 4b (CD), suggest that in DMBADC δ is also different from zero. In DHDNP the large value of ε for the *p*-band makes the spectra sensitive to changes in δ as can be easily seen in Figs 2a and 2b.

This difference in resonance interaction parameters, ε, for DMBADC and DHDNP is very interesting. If one assumes dipole-dipole type interaction, then it is easy to estimate its value, and one gets bigger ε for DHDNP [4]. The difference in these "theoretical"

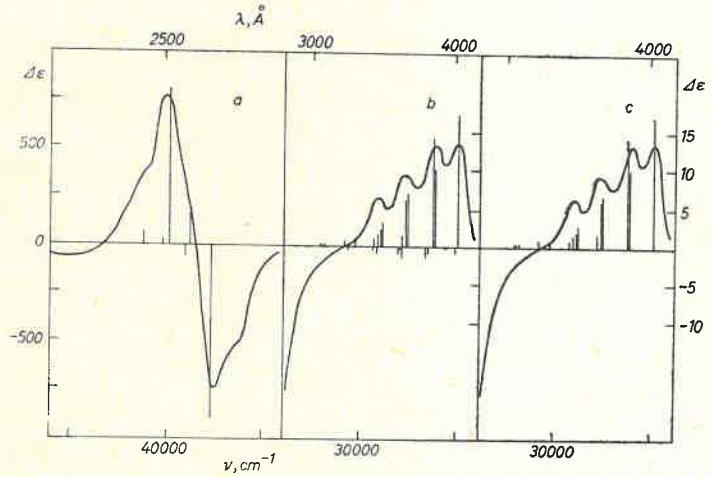

Fig. 4a. Experimental and theoretical CD spectra for β-band of DMBADC; b. Experimental and theoretical CD spectra for p-band of DMBADC ($\delta = 10°$); c. the same plot as 4b but with $\delta = 0°$

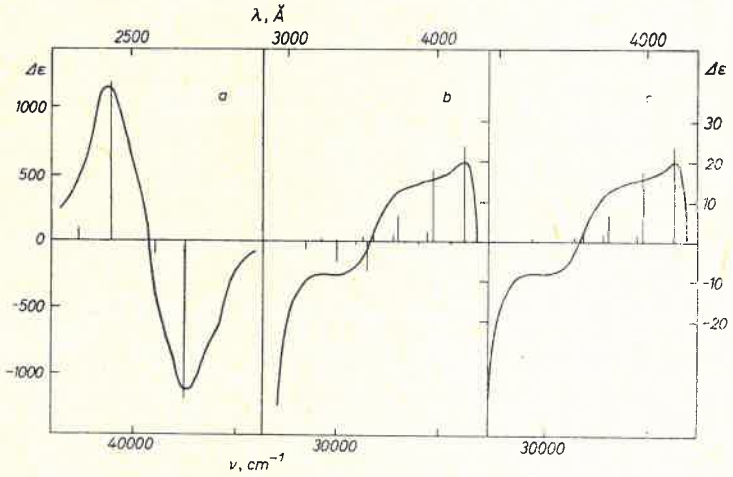

Fig. 5. The same plot as Fig. 4 but for DHDNP

values is, however, much smaller than observed. This is especially true for the p-bands, and may be connected with the interaction between π-electron systems of anthracene rings and the nonbonding electrons of the carbonyl groups. It shows also that dipole-dipole approximation breaks down in these compounds.

3. Circular dichroism and optical rotatory dispersion

According to Weigang's paper [17], the rotatory strength of the μ, ν-th vibronic level of a dimer, resulting from the magnetic moment that arises because the dipole transition moments in monomers do not lie in one plane is

$$R_{\mu\nu}^{\pm} = -Im\{\vec{M}_{\mu\nu}^{\pm} \cdot \vec{\mu}_{\mu\nu}^{\pm}\} = \mp 2c^{-1}\omega_0(\vec{M}_a\vec{R}_b \times \vec{M}_b)\,|b_{\mu 0}c_{\nu 0}^{\pm}|^2. \tag{1}$$

All symbols in (1) have just the same meaning as in [17]. Only $R_{\mu\nu}^{\pm}$ differ here in sign from those introduced by Weigang, as we difine the rotatory strength for an $a \to b$ transition as $Im\,[\langle a|\vec{M}|b\rangle\,\langle b|\vec{\mu}|a\rangle]$ and not as $Im\,[\langle a|\vec{M}|b\rangle\,\langle a|\vec{\mu}|b\rangle]$ as Weigang has done. Now, we adopt (1) to CD in β-bands. The mixed product in (1) can be easily evaluated. Because $\vec{M}_a(\vec{R}_b \times \vec{M}_b) = \vec{R}_b(\vec{M}_b \times \vec{M}_a)$ and $\vec{M}_b \times \vec{M}_a$ is parallel to the y-axis, we get for its absolute value the expression $d|\vec{M}_a|^2 \sin\alpha$ where d is one half of the projection onto the y-axis of a vector joining the centers of two anthracene rings. It is approximately equal to 1.5 times the average C–C distance at the sp^2 hybrydization. The sign of this product is positive for the S-configuration, and negative for the R-configuration (see Fig. 3). So, assuming the R-configuration we have

$$R_{\mu\nu}^{\pm}(\beta) = \pm(2c)^{-1}\omega_0 d|\vec{M}_a|^2 \sin\alpha|b_{\mu 0}c_{\nu 0}^{\pm}|^2 \tag{2}$$

for β-bands.

Therefore, the sign of circular dichroism should be plus for the plus system and minus for the minus system. A look at Figs 4a and 5a shows that this is really what one observes. We see also that the theoretical vibronic structure of CD in β-bands fits the observed spectrum quite well. In calculating this structure, we used ε and λ parameters estimated in the previous section. Now, we will concentrate on the p-bands. Circular dichroism in these bands was partially analyzed in [4]. It has been shown that the transition to the plus system of a p-band possesses a nonvanishing moment parallel to the z-axis. However, its rotatory strenght is zero because of the vanishing electric dipole moment. The minus system, on the other hand, possesses an electric dipole transition moment oriented along the y-axis, and also a weak magnetic moment parallel to the electric one, but with oposite direction. This magnetic moment is $\mu_y = \mu_0 \sin\alpha$, where μ_0 is close to 0.1 μ_B (μ_B — Bohr's magneton). Therefore, for parallel short axes of anthracene rings, circular dichroism can be present only in the minus system, and its vibronic structure should be almost the same as that in absorption, as

$$R_{\mu\nu}^{+}(p, \delta = 0) = 0, \tag{3a}$$

$$R_{\mu\nu}^{-}(p, \delta = 0) = \mu_0|\vec{M}_a| \sin\alpha|b_{\mu 0}c_{\nu 0}^{-}|^2. \tag{3b}$$

This contradicts the experiment Figs 1 and 4, 2 and 5 which is especially clearly seen for DHDNP, in which the high energy part of CD spectrum possesses the minus sign. All these suggest again that the short anthracene axes are not parallel ($\delta \neq 0$). If so, then the projections of electric dipole moments in monomers upon the xz plane will form an additional rotatory strength, the absolute value of which will be the same in both systems, and the sign of which will be positive in the minus system and negative in the plus system.

The formulae that describe rotatory strengths for vibronic transitions of a dimer with the configuration presented in Fig. 3 may be seen in the Appendix. The results are:

$$R^{+}_{\mu\nu}(p) = -(2c)^{-1}\omega_0|\vec{M}_a|^2\left[d\sin\alpha\sin^2\delta + d_0\cos\delta\sin\delta\sin\frac{\alpha}{2}\right]|b_{\mu 0}c^{+}_{\nu 0}|^2, \tag{4a}$$

$$R^{-}_{\mu\nu}(p) = \left\{\mu_0|\vec{M}_a|\sin\alpha\cos\delta + (2c)^{-1}\omega_0|\vec{M}_a|^2 \times \left[d\sin\alpha\sin^2\delta + d_0\cos\delta\sin\delta\sin\frac{\alpha}{2}\right]\right\}|b_{\mu 0}c^{-}_{\nu 0}|^2, \tag{4b}$$

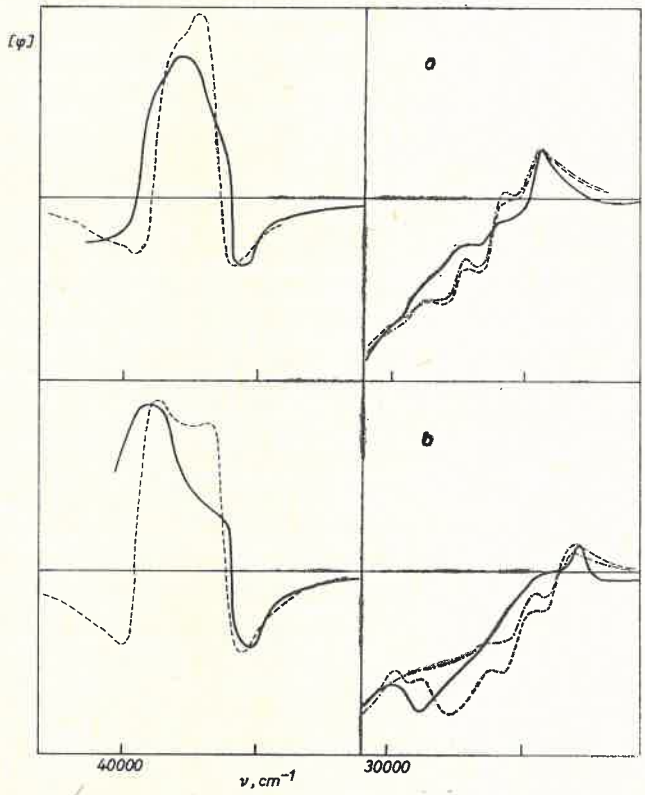

Fig. 6. Experimental and theoretical curves of ORD spectra for a. DMDADC; b. DHDNP; full line — experimental data, dashed line — theoretical curves with $\delta = 10°$, dot-dashed line — theoretical curve with $\delta = 0°$

for the plus and minus systems, respectively. d_0 denotes the distance between dipole transition moments of monomers measured in the xz-plane (Fig. 7). With the help of these equations we performed the calculation of the vibronic structure of CD spectra for p-bands.

The same value of ε, λ, α and δ parameters were used as those in the calculation of absorption spectra. The magnetic moment μ_0 was obtained by integration of CD spectra

and reads 0.1 μ_B for DHDNP and $\sim 0.2\ \mu_B$ for DMBADC. The only parameter that is difficult to estimate id d_0. Assuming, that dipole transition moments are located at centers of anthracene one gets $d_0 = 2d/\sqrt{3}$. The calculated CD spectra are shown together with

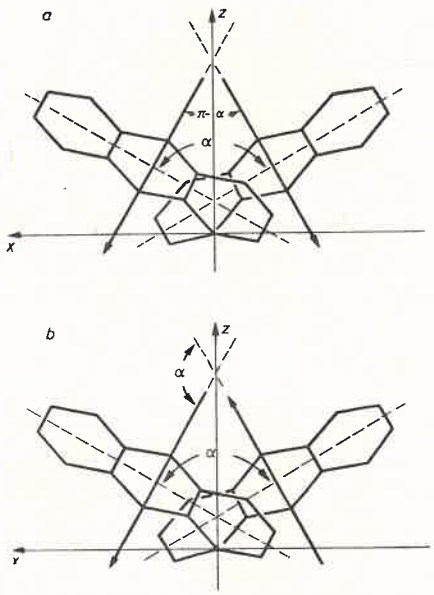

Fig. 7. The projection of two anthracene rings and transition moments in p-band onto xz-plane; a. in the plus system; b. in the minus system

the experimental one on Figs 4, 5. Figs 4c and 5c shows the theoretical predictions for $\delta = 0°$. The agreement is good, and one sees that CD spectra for DHDNP indicate very clearly that the angle δ cannot be zero.

The only discrepancy, that cannot be explained is the additional shoulder at the beginning of the β-band CD spectrum, which lies at 36200 cm^{-1} in DMBADC and at 35800 cm^{-1} in DHDNP. This shoulder is definitely not connected with vibronic structure of β and p-band, and may indicate the presence of another electronic state in this region, that may be connected with charge-transfer between anthracene rings.

The other discrepancy, is the larger experimental energy separation between the second and the third vibronic peaks in p-band of DMBADC, than that resulting from our calculations. This may be connected with the presence of weak α-band covered by the p-band [22].

We have also calculated the theoretical ORD spectra. The angle of the polarization plane rotation as a function of light frequency is given by [19]

$$\varphi(\omega) = \text{const} \cdot \text{Re} \sum_{\mu\nu} \left[\frac{\omega^2 R^+_{\mu\nu}}{\omega^{+2}_{\mu\nu} - \omega^2 - i\Gamma\omega^+_{\mu\nu}} + \frac{\omega^2 R^-_{\mu\nu}}{\omega^{-2}_{\mu\nu} - \omega^2 - i\Gamma\omega^-_{\mu\nu}} \right], \tag{5}$$

where $\omega_{\mu\nu}^{\pm}$ is the energy of the vibronic state, and Γ^{-1} is proportional to the life-time of the excited states. In principle Γ shoud be also a function of μ, ν indexes, but for simplicity we set the life time of all excited vibronic states equal to 10^{-10} s. Note, that a more realistic choice would be $\Gamma_{00}^{\pm}$ 10^{-8} s and $\Gamma_{\mu\nu}^{\pm}$ ($\mu \neq 0$, $\nu \neq 0$) $10^{-12} - 10^{-13}$ s.

The first, for the lowest excited vibronic state, is of the order of electronic relaxation time, whereas the others are of the order of vibrational relaxation time. However, in order not to introduce too many parameters, we put only one value for Γ being the geometrical average of two types of relaxation times. The calculated ORD curves are given in Fig. 4 together with experimental ones. We see that agreement in p-bands is good. Better agreement can be achieved upon introduction of two types of life times. Note, that the curves with $\delta = 10°$ better fit the experiment especially for DHDNP (maximum at 30000 cm^{-1}). The β-band ORD spectrum for DMBADC is reproduced quite well, however there is noticeable discrepancy in the shape of β-band for DHDNP (too large theoretical angle at the first maximum). This discrepancy cannot be explained within the assumed model.

4. Discussion

An interesting conclusion can be drawn from our calculations with respect to the relative orientation of anthracene rings in 1, 1′-bianthryl derivatives. We have seen that most of the properties of UV, CD and ORD spectra can be explained by the configuration presented in Fig. 3. One should, however, point out that some other effects can also influence the vibronic structure in these spectra.

One of them is possibility that the transition moments to p-state in the monomer are not parallel to short axis of a ring. This is theoretically possible because of the low symmetry of a monomer. However, it should be bigger in DMBADC, where the interaction of π-electron system with a substituent is more important than in DHDNP. The experiment shows, however, that it is DHDNP in which spectral changes are bigger, and DHDNP is the compound in which the steric effect created by ethylene bridge is stronger, suggesting the deviations of anthracene rings. Therefore, we think that the presence of the negative CD in p-band of DHDNP is connected with the fact short axes of anthracene rings are not parallel.

The second effect, that can influence the vibronic structure, is the possible vibronic borrowing of intensity between β and p-bands. However, so little is known about vibronic spectra of the true monomers of the investigated dimers, that it is not possible to go deeper into this problem.

The third effect — discussed by Frank-Kameneckij and Lukashin [20], resulting from dissymmetrical displacement of equilibrium positions of nuclei upon excitation of a molecule — does not apply to the investigated chromofores. This effect applies only to the so called II case of Moffitt and Moscowitz [1]. These authors [20] investigated an optical activity induced in a symmetrical chromofore by a dissymetrical external fields, whereas 1, 1′-bianthryls are already dissymmetrical chromofores. So, the most probable cause of the above mentioned pecularities in the spectra is the non-parallel arrangement of

the short anthracene axes. It cannot be ruled out, however, that possible vibronic interaction between β^+ and p^+ band (via a totally symmetric coordinate), that can influence rotatory strength, plays some role also.

As both effects can contribute, one should treat the estimation of δ angle as semi-quantitative only. In order to measure this angle precisely, and to find, which of these two effects plays a major role, an investigation of p-band in polarized light is necessary (with respect to UV spectra). As is shown in the Appendix, the transition to the plus system are polarized along the z-axis, and the transitions to the minus system are polarized in the xy-plane. The ratio of total intensities of these two systems is then

$$\varrho = \frac{(1-\cos 2\delta)\,(1-\cos\alpha)}{2(1+\cos 2\delta)+(1-\cos 2\delta)\,(1+\cos\alpha)}, \tag{6}$$

and its measurements allows the determination of the δ-angle.

Recently, the spectra of the third derivative, namely 2, 2′-dimethyl-1, 1′-bianthryl (DMBA) were measured [21]. Its spectra also confirm our hypothesis on the configuration presented in Fig. 3. Their analysis is, however, a little bit more complicated, as one has to take into account also the α-band, that was completely covered by the p-band in the compounds that were investigated in this paper. The analysis of DMBA UV and CD spectra will be presented elsewhere [22]. Our results sindicate, that the theory of vibronic coupling in dimers can explain satisfactorily the observed CD and ORD spectra in molecules built from two independent chromofores.

APPENDIX

The y components of the dipole transition moments for p-bands are

$$M_y^+ = 0, \quad M_y^- = 2|\vec{M}_a| \cos\delta \tag{A1}$$

for plus and minus systems, respectively. ($\vec{M}_a$ — dipole transition moment of a monomer)

As one can see from Fig. 7, their projections onto the xz-plane are

$$M_x^+ = M_z^- = 0, \quad M_z^+ = -2|\vec{M}_a| \sin\delta \sin\frac{\alpha}{2}, \quad M_x^- = 2|\vec{M}_a| \sin\delta \cos\frac{\alpha}{2}. \tag{A2}$$

So, the total intensity is

$$|\vec{M}^+|^2 = |M_z^+|^2 = |\vec{M}_a|^2(1-\cos\alpha)\,(1-\cos 2\delta) \tag{A3}$$

$$|\vec{M}^-|^2 = |M_x^-|^2+|M_y^-|^2 = |\vec{M}_a|^2[2(1+\cos 2\delta)+(1+\cos\alpha)\,(1-\cos 2\delta)].$$

The magnetic moment of the p-band have very small component along the x-axis, and these component give a vanishingly small contribution to the rotatory strength, as it is multiplied by M_x.

The μ_y^- — component give, together with M_y^- — the rotatory strength equal to

$$|R^-| = 2\mu_0|\vec{M}_a| \sin\alpha \cos\delta. \tag{A4}$$

Its sign depends on the relative orientation of the two dipole moments. It is positive for antiparallel dipole moments ($\delta = 0$). The part of the mixed product $\vec{R}_b(\vec{M}_b \times \vec{M}_a)$ that comes from the xz-planar components of two dipole moments is

$$\pm d|\vec{M}_a|^2 \sin^2 \delta \sin \alpha. \tag{A5}$$

However, the transition to the plus system possesses a magnetic moment with a z component that arises from the y-components of electric dipole transition moments in monomers (Fig. 3). This gives an additional contribution to the rotatory strength in this system, which is negative for the conformation presented in Fig. 3. In the minus system $M_y^- \neq 0$ and the z components of $\vec{M}_a$, $\vec{M}_b$ will produce a magnetic moment parallel to the y-axis. This gives also a contribution to the rotatory strength equal in absolute value to those for the plus system but with opposite sign. They read

$$c^{-1}\omega_0 d_0 |\vec{M}_a|^2 \cos \delta \sin \delta \sin \frac{\alpha}{2}. \tag{A6}$$

Summing up (A4), (A5), and (A6) one gets Eqs (4a) and (4b).

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