

# OPTICAL ACTIVITY OF MOLECULAR DIMERS: THEORETICAL ANALYSIS OF VIBRONIC CIRCULAR DICHROISM IN MODEL BIARYLS\*

BY S. CZARNIECKI

Institute of Chemistry, Jagellonian University, Cracow\*\*

AND A. WITKOWSKI\*\*\*

Section de Résonance Magnétique du Département de Recherche Fondamentale, Institut de Recherche Fondamentale, Grenoble

(Received March 15, 1977)

Theoretical analysis of the role played by the vibronic effects in the spectra of absorption and circular dichroism of some model biaryls is presented. The vibrational structure of the circular dichroism spectra was found to be highly influenced by the factors of virtually no influence on the absorption spectra which allows to determine from vibronic circular dichroism even the small geometrical and conformational changes. The theory applied to the circular dichroism spectra of some bianthryl derivatives leads to a good agreement between the theoretical and experimental vibronic spectra.

## 1. Introduction

The optical activity of molecular systems with an asymmetric configuration of the identical chromophoric units like e.g.  $\alpha$ -helical polipeptides and other biopolymers, created a considerable interest for the study of the simplest molecular models of such optically active systems. The 1,1' bianthryl derivatives form a convenient example of such intrinsically dissymmetric chromophores with a fairly strong optical activity. Some bianthryl derivatives substituted in the 2,2' positions have been recently synthesized, their UV, CD and ORD spectra obtained and corresponding bands interpreted in terms of the one-electronic transitions [1-5].

The UV and CD spectra of the bianthryl derivatives have a clear vibronic structure with a best resolution displayed by the most recent CD and UV spectra of the 2,2'-dimethyl-

\* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

\*\* Address: Instytut Chemii, Uniwersytet Jagielloński, Krupnicza 41, 30-060 Kraków, Poland.

\*\*\* On leave of absence from the Institute of Chemistry, Jagellonian University, Cracow, Poland.

-1,1'-bianthryl (DMBA) obtained by Ito and Hatano [2]. The aim of our paper is the theoretical analysis of the vibronic structure in the CD and UV spectra of DMBA in relation to its geometrical structure. The quantitative analysis of the vibronic spectra will be shown to allow for a precise determination of the relative configuration of the interacting chromophoric units formed in DMBA by the two substituted anthracene units.

The 1,1' bianthryl derivatives to a good approximation may be treated as the anthracene dimers which allows for an application of the theory of vibronic coupling in dimers formulated by Witkowski and Moffitt [6, 7], and developed later by Fulton and Gouterman [8]. This vibronic theory applied by Weigang [9] to dimeric optically active systems in the model calculations led to the conclusion of the identical vibronic structure in the CD and the corresponding absorption spectra.

Our theoretical analysis of the experimental vibronic absorption and CD spectra of DMBA differs from the model calculations in both the theoretical and practical aspects. On the theoretical side we will show that the  $\alpha$ -electronic transition in the anthracene unit which is of virtually no influence on the vibronic structure of the UV absorption influences profoundly the vibronic structure of the corresponding CD spectra. On the practical side we will show how the vibronic structure of the CD spectrum can serve as a sensitive tool for determining the minor conformational changes in the relative positions of the chromophoric units. On the other hand the vibronic CD spectra of a dimer may therefore be useful for determining the positions and intensity of the weak or overlapping electronic transitions in the UV absorption spectra of the component monomer. In terms of the exciton model in the Born-Oppenheimer approximation an interpretation of the electronic spectra of some other bianthryl derivatives: dimethyl 1,1' bianthryl 2,2' dicarboxylate (DMBAC) and 9,10-dihydrodinaphtho (2',3'-3,4:2'',3''-5,6)-phenanthrene (DHDNP) was given by Grinter and Mason [4]. They have confirmed the absolute configuration of this compounds and determined the angle between the long anthracene axes from the spectra corresponding to the  $\beta$ -type transition in the aromatic ring. The value of the angle formed by the short anthracene axes was not determined and was supposed equal  $0^\circ$ .

Theoretical analysis of the vibronic structure of the UV, CD and ORD spectra of this two (DMBAC, DHDNP) bianthryl derivatives was formulated very recently [10]. The vibrational structure of the CD and ORD spectra corresponding to the  $p$ -type transition was shown to determine the details of the geometrical structure and allowed to determine the angle between the short anthracene axes [10].

## 2. Absorption spectra

The anthracene absorption spectrum in the range of 2000-4000 Å corresponds to two well characterised electronic transitions [11, 12]. The higher energy transition near  $39000\text{ cm}^{-1}$  of the  ${}^1A_{1g} \rightarrow {}^1B_{3u}$  type, or  $\beta$  in the Clar's [13] classification, is polarized along the longer in-plane molecular axis. The other transition, near  $27000\text{ cm}^{-1}$ , of the  ${}^1A_{1g} \rightarrow {}^1B_{2u}$ , or  $p$ -type, has a well developed vibration alstructure and is polarized along shorter molecular axis.

In dimers each monomeric  $\beta$  or  $p$  electronic transition splits leading to two series ( $\pm$ ) of vibronic transitions [7, 8] which also will be denoted by  $\beta$  and  $p$ —as the corresponding anthracene transitions. The totally symmetric C—C stretching mode determines the vibrational structure of the anthracene absorption and the influence of the other vibrations is negligible [14].

It follows from the theory of vibronic coupling in dimers [6–8] that frequency and intensity of the vibronic transitions are determined by the following basic parameters:  $\lambda$ —a distortion parameter describing the change of the nuclear equilibrium position after the electronic excitation,  $\epsilon$ —the resonance coupling parameter describing the interaction between the monomers and  $\alpha$ —the angle between the dipole transition moments in the monomers. This theory can be directly applied to the  $\beta$ -transitions and the intensity of the  $\mu$ ,  $\nu$ -th vibronic absorption component is equal [10]

$$I_{\mu\nu}^{\pm} = D(1 \pm \cos \alpha) (b_{\mu 0} c_{\nu 0}^{\pm})^2, \quad (1)$$

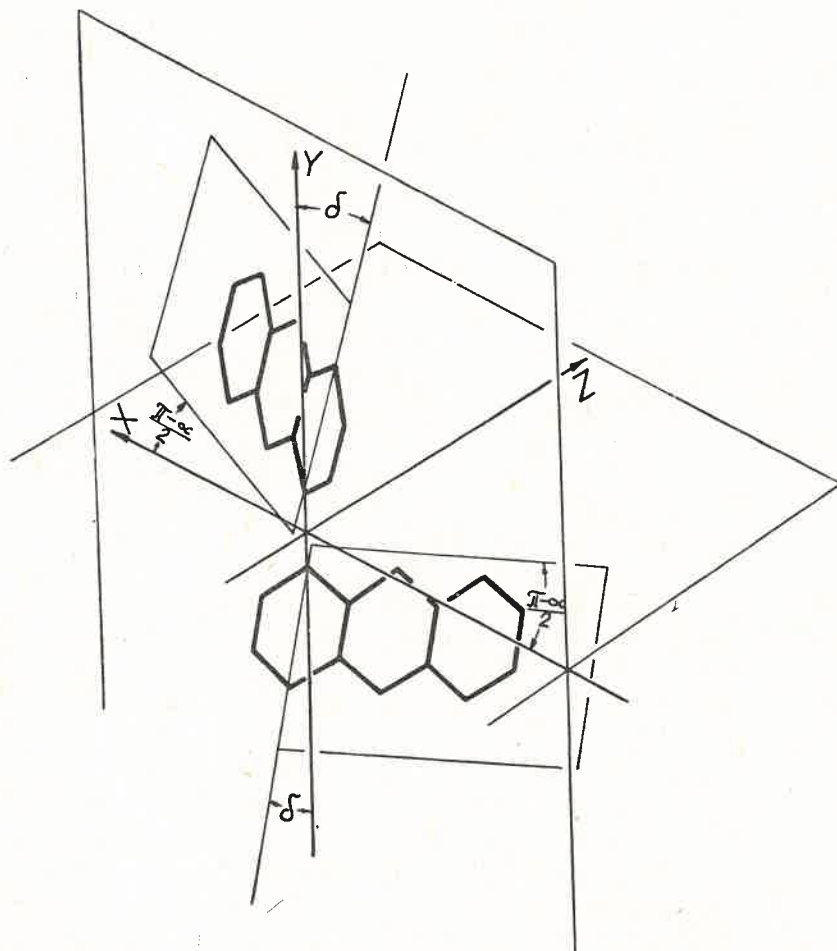


Fig. 1. The geometry of the bianthryl derivatives

where  $D$  is the moment of the zeroth order of the monomeric spectrum and the  $b_{\mu\sigma}$ ,  $c_{\mu\sigma}^{\pm}$  are the corresponding vibrational overlap integrals and  $\mu, \nu$  denote the totally and non-totally symmetric vibrations respectively and  $\alpha$  is the angle between the long anthracene axes.

For the  $p$ -band the intensity will depend also on the angle  $2\delta$  between the shorter anthracene axes (Fig. 1) and equals [10]

$$I_{\mu\nu}^+ = 0.5D(1 - \cos \alpha)(1 - \cos 2\delta)(b_{\mu\sigma}c_{\nu\sigma}^+)^2, \quad (2)$$

$$I_{\mu\nu}^- = D[(1 + \cos 2\delta) + 0.5(1 + \cos \alpha)(1 - \cos 2\delta)](b_{\mu\sigma}c_{\nu\sigma}^-)^2. \quad (3)$$

The theoretical absorption spectra calculated by an application of the above given formulae are represented on Fig. 2. Comparison of the calculated spectra with the experimental ones allowed to determine the values of the fundamental vibronic parameters  $\lambda$  and  $\varepsilon$ . The values of  $\lambda$  and  $\varepsilon$  are found equal 0.4 and 0.5 correspondingly, for the  $\beta$ -band

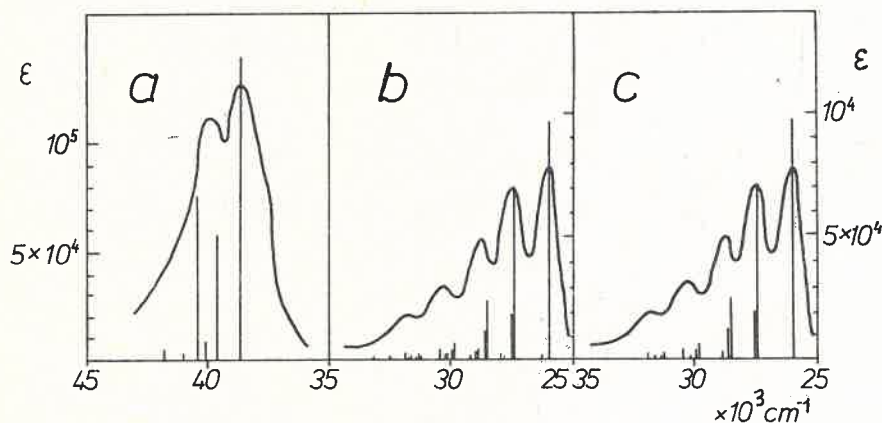


Fig. 2. The absorption spectrum of DMBA and its theoretical reconstitution in terms of linear spectra: a) the  $\beta$ -band, b) the  $p$ -band and spectra calculated for the angle  $2\delta$  between the short axes with  $\delta = 10^\circ$ , c) the  $p$ -band and spectra computed for  $\delta = 0^\circ$

and 1.2 and 0.7 for the  $p$ -band. The best fit with the experimental spectrum was found for the frequency of the fundamental vibration equal  $1300 \text{ cm}^{-1}$ , which is somewhat lower than the corresponding vibration of  $1400 \text{ cm}^{-1}$  frequency in an anthracene moiety. This slight frequency decrease is probably introduced by the increase of the effective mass resulting from the substitution of the  $\text{CH}_3$  group in the position 2.

For the  $\beta$ -transition the angle  $\alpha$  between the long axes dipole transition moments determined from the relative intensities of the vibronic transitions is equal  $91^\circ$  (Ito and Hatano [2] evaluated  $\alpha = 100^\circ$ ). On the other hand the absorption spectrum displays a rather small sensitivity to the changes of the  $\delta$ -angle excluding therefore its precise determination (in contrast to the CD spectra — as will be shown a little later). The value of  $\delta = 10^\circ$ , used by us before for the case of other bianthryls [10], leads to a fair agreement with the experimental absorption spectra.

### 3. Circular dichroism spectra

In the bianthrils both the  $\beta$  and  $p$ -bands are optically active. The optical activity of  $\beta$ -band results from the charge rotation during the excitation transfer between the anthracene moieties [4, 10] and as shown in [10] the rotational strength  $R_{\mu\nu}^{\pm}$  of the  $\mu, \nu$  vibronic component for the  $R$  configuration in the dimer is equal

$$R_{\mu\nu}^{\pm} = \pm(2c)^{-1}\omega_0 D d \sin \alpha (b_{\mu_0 c_{\nu_0}^{\pm}})^2, \quad (4)$$

where  $d$  is a mean carbon-carbon distance in the  $sp^2$  hybridization and  $\omega_0$  is the mean circular frequency of transition.

For the  $p$ -band there are two contributions to the optical activity. On the one hand there is a nonvanishing magnetic moment  $\mu_z$  along the  $z$ -axis,  $\mu_z = \mu_0 \sin \alpha$  which accompanies the spectral transition to the minus system. On the other hand we have a moment resulting, in an analogous manner as in the  $\beta$ -transition, from the corresponding components of the electric dipole moments in the anthracene monomeric units. As shown in [10] the corresponding vibronic components of the rotational strength are equal

$$R_{\mu\nu}^+ = -(2c)^{-1}\omega_0 D \left[ d \sin \alpha \sin^2 \delta + d_0 \cos \delta \sin \delta \sin \frac{\alpha}{2} \right] (b_{\mu_0 c_{\nu_0}^+})^2, \quad (5)$$

$$R_{\mu\nu}^- = \left[ \mu_0 D^{1/2} \sin \alpha \cos \delta + (2c)^{-1}\omega_0 D \left( d \sin \alpha \sin^2 \delta + d_0 \cos \delta \sin \delta \sin \frac{\alpha}{2} \right) \right] (b_{\mu_0 c_{\nu_0}^-})^2, \quad (6)$$

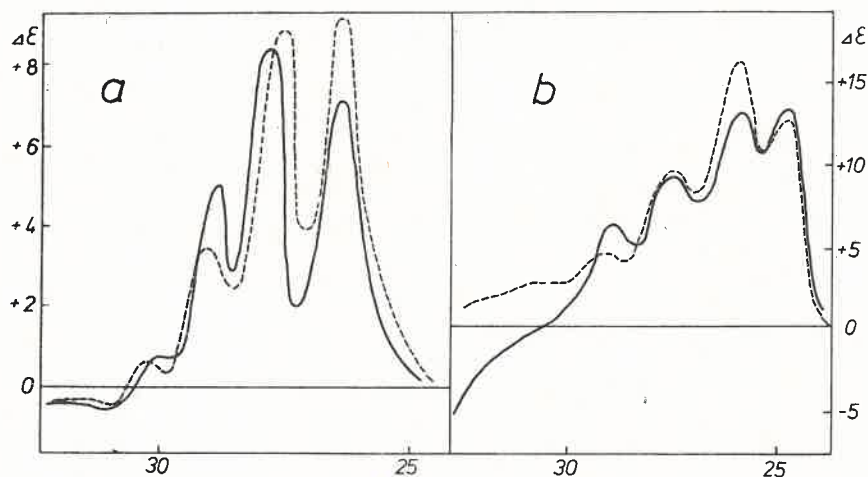


Fig. 3. The experimental CD spectrum (continuous lines) corresponding to  $p$ -band and its theoretical reconstitution (broken lines) calculated in terms of the gaussian linewidth with angle  $\delta = 10^\circ$ : a) DMBA, b) DMBADC

where  $d_0$  denotes the distance between the electric dipole moments in the monomeric units in the  $XZ$  plane. The value of  $\mu_0$  determined from the integration of the CD spectrum equals about  $0.1 \mu_B$ .

The above given formulae of the rotational strength allow to calculate the theoretical CD spectra in terms of the vibronic parameters determined from the absorption spectra. Using the values of this parameters  $\lambda$ ,  $\epsilon$  determined in the previous section from the absorption spectrum we have obtained the CD spectra presented on Fig. 3. Not only the intensity but even the frequency distribution of the vibronic structure of the calculated spectra differ substantially from the experimental ones.

#### 4. Discussion

Comparison of the theoretical and experimental absorption spectra presented on Fig. 2 shows a good agreement of the calculated spectra with the experimental ones for both the frequency and the intensity distribution of the vibronic structure. For the  $p$ -type transition the calculated intensities of the higher frequency components of the vibronic structure are however somewhat lower than the experimental ones. Similar lower values were obtained for some other anthracene dimers [10, 14] and this small intensity differences can be removed by taking into account the change of the force constants after the electronic excitation, a change which we neglected here for simplicity. For the  $\beta$ -type absorption spectrum only a very small shoulder at the  $37500\text{ cm}^{-1}$  is not accounted for by the adopted model.

For the circular dichroism spectra the comparison of the calculated and experimental spectra leads however to different conclusions. The CD spectra calculated for DMBA as well as for DMBADC with the use of the corresponding vibronic parameters determined from the absorption spectra differ substantially from the experimental ones not only in the intensity but even in the frequency distributions (Fig. 3).

This discrepancy seems to be related to the  $\alpha$ -type transition in the anthracene monomeric unit of bianthrils, which is a very weak one but located in the same region as the  $p$ -type transition. This weak transition will split in two components in the dimer which are additive in the absorption intensity but are subtractive in the CD spectra changing therefore sign in a relatively narrow frequency range. In the anthracene monomer this  $\alpha$ -type transition is covered by the more intense  $p$ -type one and we are therefore obliged to use for the  $\alpha$ -transition the theoretical values [15, 16] for the frequency and intensity, the last being an order of magnitude lower than in the  $p$ -type. We are supposing also the same values of the vibronic parameters for  $\alpha$  as for the  $\beta$ -type transitions owing to a similarity of this transitions in relation to the same  $B_{3u}$  symmetry of the generating electronic level in the monomer.

For the DMBA the calculated vibronic CD spectra which include the  $\alpha$ -type transition are presented on Fig. 4a. The similar theoretical vibronic CD spectra including  $\alpha$ -type transition for another bianthrill derivative: DMBADC are presented on Fig. 4b. For this last compound we have used in calculations the vibronic absorption parameters which we have recently determined [10].

The calculated circular dichroism spectra are now in a very good agreement with the experimental ones for both the frequency and intensity distribution of the vibronic fine structure, giving therefore a strong support for the important role played by the

$\alpha$ -type transitions in the CD spectra. In the bianthryls the much more intense  $p$ -type transition of the anthracene unit covers the  $\alpha$ -one and information concerning its exact position and intensity is only indirectly available. In the monomeric units of the other biaryls the  $\alpha$ -type transition will be less covered by the  $p$ -type and the high resolution CD

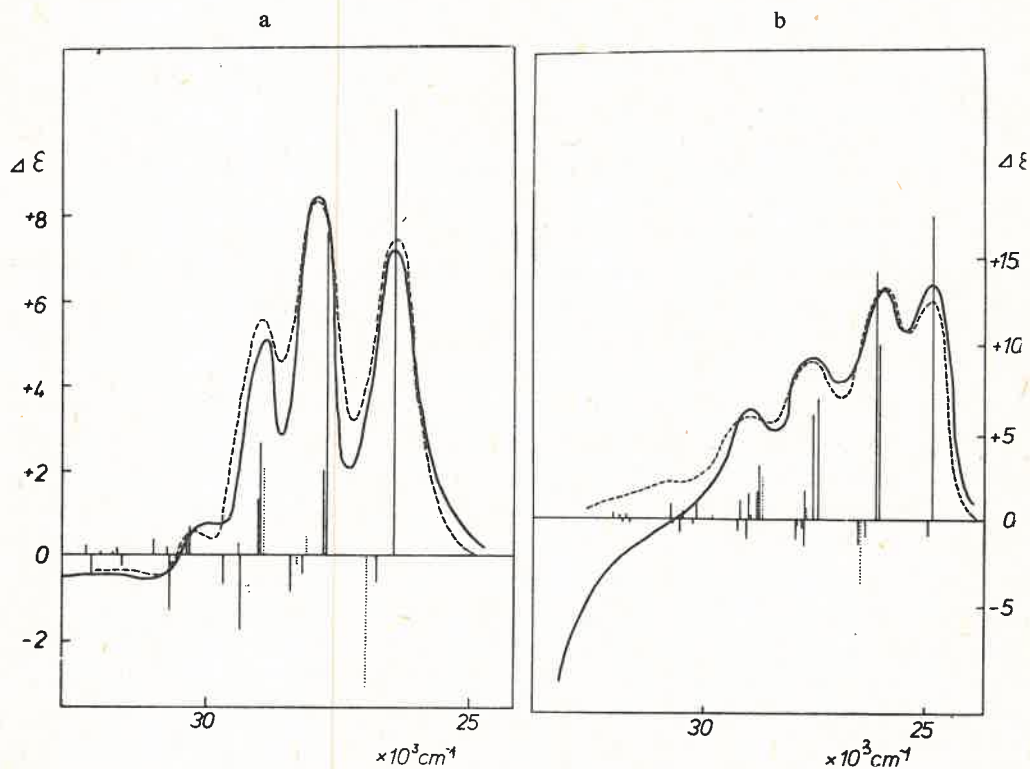


Fig. 4. The experimental CD spectrum (continuous lines) corresponding to  $p$ -band and its theoretical reconstitution (broken lines) in terms of the gaussian linewidth with inclusion of the  $\alpha$ -type band and with angle  $\delta = 10^\circ$ . The dotted vertical lines denote the contributions to CD originating from the  $\alpha$ -band: a) DMBA, b) DMBADC

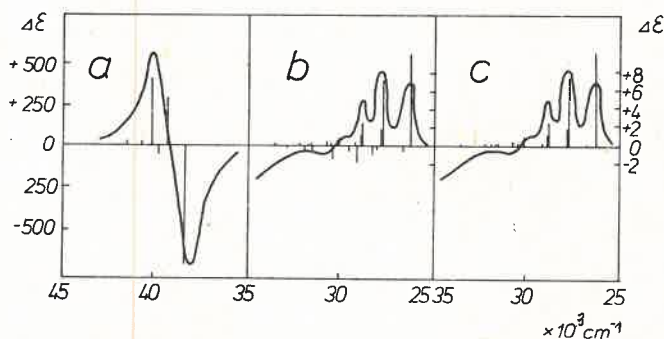


Fig. 5. The experimental CD spectra and corresponding theoretical reconstitution in terms of linear spectra: a) the  $\beta$ -band, b) the  $p$ -band,  $\delta = 10^\circ$ , c) the  $p$ -band,  $\delta = 0^\circ$

spectra of such systems would be very useful for the definite confirmation of our conclusions concerning the important role of the  $\alpha$ -transitions in the optical activity.

Comparison of the calculated and experimental spectra corresponding to the  $p$ -type transition in absorption and CD leads to an interesting observation. The calculated vibronic fine structure of the absorption spectrum remains practically unchanged when the angle  $2\delta$  formed by the short anthracene axes is changed in DBMA from  $\delta = 0^\circ$  (Fig. 2c) to  $\delta = 10^\circ$  (Fig. 2b). On the contrary the corresponding vibrational structure in the CD spectra is very sensitive to the variation of the angle between the short anthracene axes. The negative high energy tail of the experimental CD spectrum can only be reproduced when the short axes in DMBA are no more parallel and form an angle  $2\delta$  with  $\delta$  equal about  $10^\circ$  (Fig. 5b).

We conclude therefore that vibrational fine structure of the optical activity contains important geometrical information which is not available from the purely electronic CD or vibronic absorption spectra. The high sensitivity of the vibrational fine structure in the CD spectra to the small conformational changes in the relative orientation of the chromophoric units seems to be of particular importance.

The quantitative analysis of the vibrational fine structure of the high resolution vibronic CD spectra may be of great value in determining the conformational changes in biopolymers and in particular in enzymes where their unusual catalytic activity is believed to result [17] from the very precise conformational changes of the catalytic subunits during the chemical reaction.

#### REFERENCES

- [1] S. M. Badger, R. Jeffers, D. P. Kimber, *J. Chem. Soc.* **1957**, 1837.
- [2] O. Ito, M. Hatano, *J. Am. Chem. Soc.* **96**, 4375 (1974).
- [3] S. M. Badger, R. J. Brewer, G. E. Lewis, *J. Chem. Soc.* **1962**, 4268.
- [4] R. Grinter, S. F. Mason, *Trans. Faraday Soc.* **60**, 274 (1964).
- [5] D. D. Fitts, M. Siegel, K. Mislow, *J. Am. Chem. Soc.* **80**, 480 (1958).
- [6] A. Witkowski, W. Moffitt, *J. Chem. Phys.* **33**, 872 (1960).
- [7] A. Witkowski, *Roczniki Chem.* **35**, 1399, 1409 (1961).
- [8] R. Fulton, M. Gouterman, *J. Chem. Phys.* **35**, 1059 (1961); *J. Chem. Phys.* **41**, 2280 (1964).
- [9] O. E. Weigang, *J. Chem. Phys.* **43**, 3609 (1965).
- [10] S. Czarniecki, A. Witkowski, M. Zgierski, *Acta Phys. Pol.* **51**, 451 (1977).
- [11] J. W. Siedman, *J. Chem. Phys.* **25**, 115 (1956).
- [12] D. P. Craig, P. C. Hobbins, *J. Chem. Soc.* **1955**, 539, 2309.
- [13] E. Clar, *Aromatische Kohlenwasserstoffe*, Springer-Verlag, Berlin 1952.
- [14] E. A. Chandross, J. Fergusson, E. G. Mc Rae, *J. Chem. Phys.* **45**, 3546 (1966).
- [15] R. Pariser, *J. Chem. Phys.* **24**, 250 (1956).
- [16] N. S. Ham, K. Ruedenberg, *J. Chem. Phys.* **25**, 13 (1956).
- [17] D. E. Koshland, IUPAC Seventh International Symposium on the Chemistry of Natural Products, Riga 1950, Butterworths, London, p. 119.