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Transannular Interactions in *Syn*- and *Anti*- [2.2](1,4) Napthalenophanes and *Syn*- and *Anti*- [2.2](1,4) Anthracenophanes

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The UV spectra of the title compounds were interpreted as a result of *PPP*-CI-1 calculations of excitation energies and oscillator strengths for the singlet—singlet transitions. A good agreement of the theoretical transitions with the experimental spectrum was found. A strong transannular effect was characteristic for the *syn* isomers, the effect decreased in the order: *syn*-ring anthracenophane, *syn*-ring naphtalenophane, *anti*-ring naphthalenophane, *anti*-ring anthracenophane. Also the influence of a pseudo-substituent effect was found and discussed.

(Keywords: [2.2] (1,4) Anthracenophanes; CT transitions; Electronic spectra; [2.2] (1,4) Naphtalenophanes; Pseudo-substituent effect; Trans-annular interactions)

Transannulare Wechselwirkungen in syn- und anti- [2.2](1,4) Naphthalenophanen und syn- und anti- [2.2](1,4) Anthracenophanen

Die UV-Spektren der Titelverbindungen wurden mittels *PPP*-CI-1-Rechnungen interpretiert; dabei wurde eine gute Übereinstimmung der theoretischen Übergänge mit den experimentellen Spektren gefunden. Für die *syn*-Isomeren wurde ein starker transannularer Effekt festgestellt, dessen Einfluß in der Reihe *syn*-Ring Anthracenophan, *syn*-Ring Napthalenophan, *anti*-Ring Naphthalenophan, *anti*-Ring Anthracenophan abnimmt. Ebenso wurde ein pseudo-Substituenten-Effekt gefunden und in die Diskussion miteinbezogen.

Introduction

We present a theoretical consideration of the transannular interaction in some [2.2]naphthalenophanes and [2.2]anthracenophanes, based on theoretical interpretation of their UV spectra. The considered structures

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were: *syn*-ring and *anti*-ring [2.2](1,4)naphthalenophanes[1,2] and *syn*-ring and *anti*-ring [2.2](1,4)anthracenophanes[3,4] (Fig. 1). Difficulties[5–9] which we already have discussed in papers concerning quinolinophanes[10] and phenyl derivatives of [2.2]paracyclophane[11] appeared in connection with calculations of the excitation energy by semiempirical quantum methods. Reason for these difficulties is that the phanes, as layered molecules, do not fulfill all conditions required for the introduction of the *Born-Oppenheimer* approximation. However, if the main objective of the calculations are excitation energies, it is possible to take into account all vibronic effects by adopting a special procedure for the evaluation of the resonance integral.

A critical step is a choice of a proper procedure to evaluate the resonance and *Coulomb* integrals, in particular the integrals between the $2p_z$ orbitals belonging to two different moieties. Following our treatments[5,10,11], we applied the *Hinze-Beveridge* parametrization[12] in a modification[10] which appeared to be very effective in the calculation of electronic spectra of cyclophanes. The application of a new empirical parameter is fully justified in case of the layered compounds, as documented by *Vogler*[13].

Materials and Methods

The investigated *syn*- and *anti*-ring[2.2](1,4)naphthalenophanes were obtained according to *Cram* et al.[1,2]. The UV spectra were recorded for the solutions in cyclohexane on the UV-Vis 5240 Beckmann and Specord UV-Vis C. Zeiss spectrometers.

The values of excitation energy of the cyclophane chromophores were calculated by a *PPP*-CI-1 method in *Hinze-Beveridge* parametrization in the same way as previously[10]. For the C parameter, see equ. (1) in[10], we adopted $C = C_{\text{H—B}}$ for all orbitals belonging to the same aromatic unit, and $C = 5\,C_{\text{H—B}}$ for orbitals of different aromatic units. In the case of 1,4-dimethylnaphtalene, *DMN*, and 1,4-dimethylanthracene, *DMA*, considered as reference molecules of cyclophane moieties, we used $\omega = -10.00$ eV for the valence state ionization potential (VSAP) of the two carbon atoms connected with the CH_3 groups, instead of the usually accepted value of $\omega = -11.16$ eV. This was done in order to account for hyperconjugation effects. As a basis for the geometry parameters we used the structure of *syn*-ring [2.2](1,4)anthracenophane[3,14]. In particular, we adopted the bond distances, angles, interplanar distances, a degree of boat-type bending in a[2.2]paracyclophane-type structural unit, and deviations from planarity of the remaining structural fragments (Fig. 2).

The analysis of the LCAO coefficients leads to a conclusion that each MO of the dimer, C_i, is characterized by a vector representing an in-phase $(+i)$ and out-of-phase $(-i)$ combination of two vectors of the corresponding chromophores

$$\mathbb{C}_j(+i) = \begin{pmatrix} \mathbb{C}_i^{ch} \\ \mathbb{C}_i^{ch} \end{pmatrix} \qquad \mathbb{C}_k(-i) = \begin{pmatrix} \mathbb{C}_i^{ch} \\ -\mathbb{C}_i^{ch} \end{pmatrix} \tag{1}$$

This means that two MO's of a dimer correspond to each MO of a monomer. This results also in a split of a single excitation of a MO of a monomer into four orbital excitations of a dimer. From the point of view of the VB theory each electronic transition may be expressed as a combination of the electronic excitations within the monomeric moiety (LE) and between the two moieties (CT).

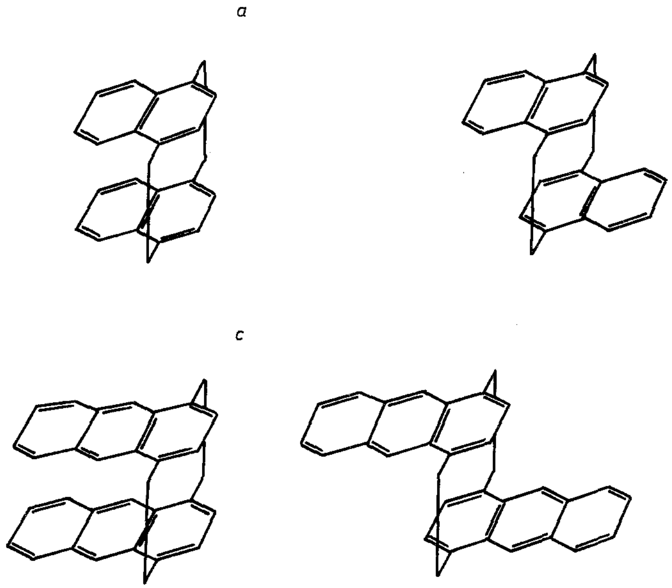

Fig. 1. Considered isomers of naphthalenophane and anthracenophane: *a syn*-ring [2.2](1,4)naphthalenophane; *b anti*-ring [2.2](1,4)naphthalenophane; *c syn*-ring [2.2](1,4)anthracenophane; *d anti*-ring [2.2](1,4)anthracenophane

Results

The recorded spectra of naphthalenophanes and the spectra of anthracenophanes[3] on which the calculations were based are presented in Fig. 3 together with the simulated spectra. The results of the calculations for the conformations assumed are presented in Tables 2 and 3. The tables contain absorption maxima and oscillator strengths related to the experimental data and the split of energy levels of the chromophores, see also Table 1. The data refer to the structures b and c shown in Fig. 2.

Discussion

There is a reasonably good agreement between the theoretical and experimental spectra of the *syn*- and *anti*-ring napthalenophanes and for the *syn*-ring anthracenophane (see Fig. 3). Energies of the electronic

Table 1. *Characteristics of some selected transitions in naphthalene and anthracene*

No.	Sym.	Energy, nm calc.	exp.[15]	Oscill. strength calc.	exp.[15]	Type	Characteristics[a]
				Naphthalene			
1	B_{3u}	307.1	297-320	0.050	0.030	α	52 (5,7), 44 (4,6), 2 (3,9)
2	B_{2u}	277.6	266-286	0.610	0.562	p	92 (5,6), 8 (4,7)
3	B_{3u}	207.5	217-221	2.130	11.70	β	54 (4,6), 45 (5,7)
4	B_{2u}	196.2	199-210[12]	1.246		β′	89 (4,7), 8 (5,6), 2 (3,8)
				Anthracene			
1	B_{2u}	351.8	323-374	0.613	0.799	p	95 (7,8), 4 (6,9)
2	B_{3u}	337.9		0.079		α	52 (7,9), 41 (6,8), 3 (5,11)
3	B_{3u}	231.3	246-252	2.401	21.80	β	54 (6,8), 42 (7,9), 2 (3,10)
4	B_{2u}	198.2	210-221	1.072	1.148	β′	79 (6,9), 12 (4,8), 4 (7,8)

[a] Participation of transitions between naphthalene and anthracene MO's.

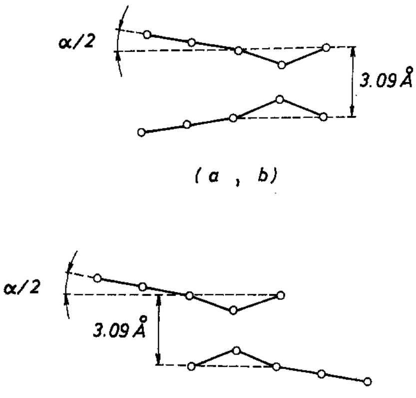

Fig. 2. Assumed geometry of the *syn*- and *anti*-ring [2.2](1,4)anthracenophanes: *a syn* isomer. $\alpha/2 = 2.5°$; *b syn* isomer, $\alpha/2 = 4.5°$; *c anti* isomer, $\alpha/2 = 0°$; *d anti* isomer, $\alpha/2 = 4.5°$. For the *syn*- and *anti*-ring [2.2](1,4) naphthalenophanes the same geometry was assumed. The distance between the aromatic planes, $l = 3.09$ Å[14]

transitions were calculated by considering 50 single-excited configurations of the singlet—singlet type. It is obvious, however, that only the energetically lowest transitions are of interest for the interpretation of the experimental UV spectra. Sixteen of the latter, originating from the fourfold splitting of the α, p, β, and β' bands (*Clar* notation) of the naphthalene and anthracene molecules are presented in Tables 2 and 3.

Table 2. *Splitting of naphthalene energy levels by the transannular interaction in the syn-ring [2.2](1,4)naphthalenophane and anti-ring [2.2](1,4)naphthalenophane*

Naphthalene	*Syn*-ring naphthalenophane							*Anti*-ring naphthalenophane						
Transition energy, nm calc.	Sym.	Transition energy, nm calc.	Transition energy, nm exp.	Oscillator strength calc.	Oscillator strength exp.	No. of band in Fig. 3	LE/CT[a]	Sym.	Transition energy, nm calc.	Transition energy, nm exp.	Oscillator calc.	Oscillator exp.	No. of band in Fig. 3	LE/CT[a]
301.7 (α)	B_2	398.9		0.017		2	49/48	A_g	352.2		0		2	24/74
	A_1	312.2	297.0	0.161	0.174	4	10/86	A_g	291.5		0		4	43/53
	A_1	206.0		0.855		15	75/14	B_u	219.3	218.0	1.815	1.202	13	6/57
	B_2	169.9		0.094		28	58/39	B_u	210.8		0.421		15	81/2
277.6 (p)	A_2	488.5		0		1	53/43	B_g	427.5		0		1	51/46
	B_1	280.8	286.5	0.416	0.151	6	53/25	A_u	283.3	286.0	0.399	0.117	5	62/25
	B_1	234.6		0.188		11	9/59	A_u	255.3	247.0	0.170	0.724	7	18/68
	A_2	177.8		0		24	40/53	B_g	193.7		0		17	18/30
207.5 (β)	B_2	317.9	311.0	0.069	0.058	3	42/58	B_u	304.5	312.5	0.101	0.120	3	3/90
	A_1	236.5	245.5	0.784	0.236	10[b]	49/16	B_u	247.3	239.0	0.627	0.758	8[b]	58/16
	A_1	180.8		1.959		20[b]	27/52	A_g	191.2		0		18[b]	26/22
	B_2	177.8		0.003		23[b]	63/27	A_g	173.1		0		26	52/28
196.2 (β')	A_2	269.4		0		7	49/26	B_b	259.4		0		6	60/18
	B_1	207.9	223.0	1.212	1.698	14	26/30	A_u	212.6	213.0	1.062	1.122	14	48/8
	B_1	180.0		0.828		21	24/51	A_u	174.8		0.892		25	13/53
	A_2	165.7		0		29	32/59	B_g	163.0		0		32	9/33

[a] Participation of the local excited, LE, and charge transfer, CT, transition; [b] bands originating from 1,4-dimethylnaphthalene, *DMN*.

Table 3. *Splitting of anthracene energy by the transannular interaction in the syn-ring [2.2](1,4)anthracenophane and anti-ring [2.2](1,4)anthracenophane*

Anthracene	*Syn*-ring anthracenophane							*Anti*-ring anthracenophane						
Transition energy, nm calc.	Sym.	Transition energy, nm calc.	exp.	Oscillator strength calc.	exp.	No. of band in Fig. 3	LE/CT[a]	Sym.	Transition energy, nm calc.	exp.	Oscillator strength calc.	exp.	No. of band in Fig. 3	LE/CT[a]
351.8 (p)	A_2	553.5	487.8	0		1	50/46	B_g	451.2	418.4	0	0.009	1	41/47
	B_1	320.1		0.557		6	57/32	A_u	319.3	396.1	0.604	0.060	3	11/79
	B_1	278.4	265.0	0.356	0.104	8	26/61	A_u	298.1	283.3	0.281	1.300	5	76/9
	A_2	221.0		0		17	32/46	B_g	292.8		0		6	9/34
337.9 (α)	B_2	406.8	408.2	0.059	0.010	2	70/26	A_g	345.0	404.0	0	0.080	2	47/50
	A_1	321.6	303.0	0.168	0.057	5	88/6	B_u	315.9	333.4	0.062	0.020	4	46/45
	A_1	200.2		3.117		26	73/22	B_u	213.1		0.620		17	16/59
	B_2	189.2		0.086		31	28/55	A_g	204.2		0		20	32/19
231.3 (β)	B_2	332.1	373.2	0.115	0.085	4	58/38	A_g	286.0		0		7	55/35
	A_1	248.9	246.0	0.997	1.060	12[b]	16/54	B_u	253.2		0.704		10[b]	47/11
	A_1	224.8		0.513		16[b]	3/82	B_u	240.6		2.620		12[b]	42/45
	B_2	196.2		0.049		28	17/35	A_g	185.2		0		27	17/42
198.2 (β′)	A_2	258.6		0		10	62/18	B_g	240.0		0		13	53/13
	B_1	206.6		1.230		24	19/19	A_u	203.1		1.645		21	35/5
	B_1	182.9		0.918		35	22/48	A_u	181.0		0.566		30	9/43
	A_2	171.6		0		42	22/53	B_g	177.2		0		32	15/31

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[a] Participation of the local excited, LE, and charge transfer, CT, transitions; [b] bands originating from 1,4-dimethylanthracene, *DMA*.

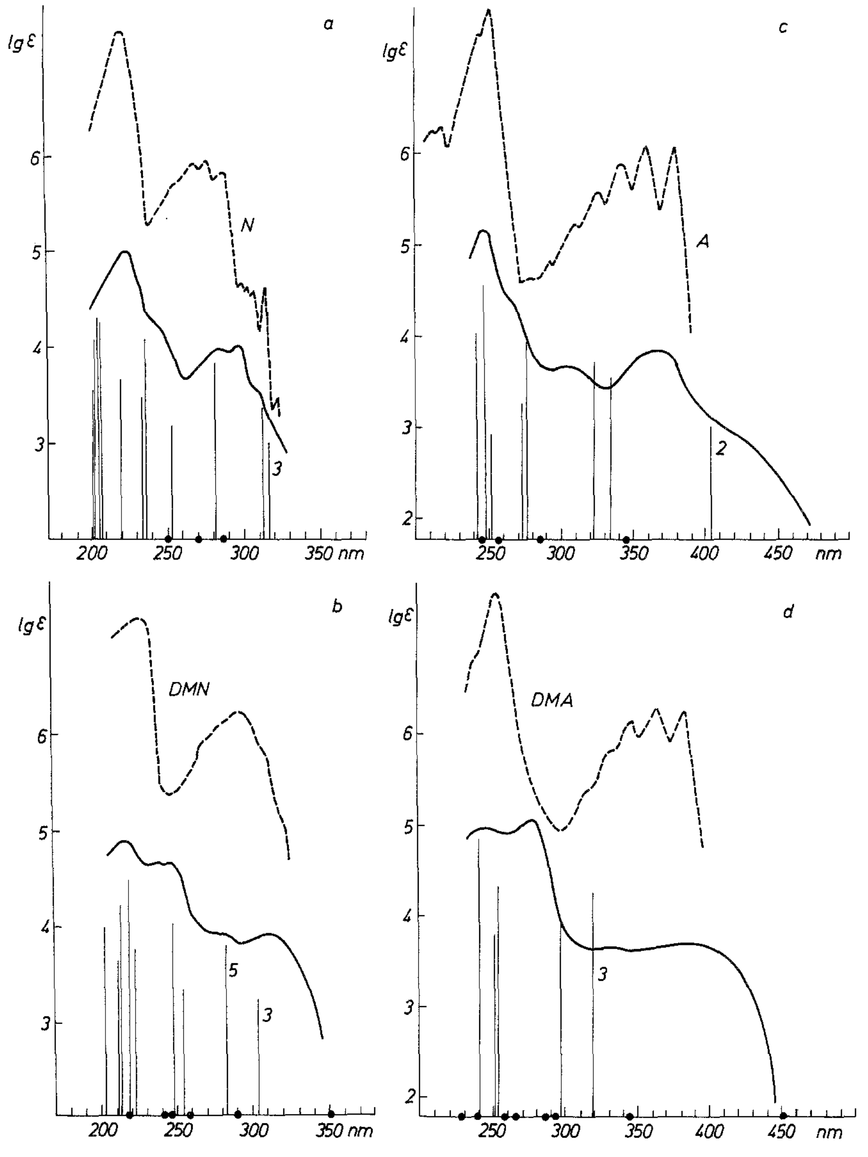

Fig. 3. Comparison of the experimental and theoretical electronic spectra for: *a* *syn*-[2.2](1,4)naphthalenophane; *b* *anti*-[2.2](1,4)naphtalenophane; *c* *syn*[2.2](1,4)anthracenophane; *d* *anti*-[2.2](1,4)anthracenophane. Theoretical bands are shown in a sequence from the marked band toward the short-wave bands (some bands are out of the presented range). Dotted lines show the experimental spectra[15] of naphthalene (*N*), 1,4-dimethylnaphthalene (*DMN*), anthracene (*A*) and 1,4-dimethylanthracene (*DMA*)

Effects of Changes in Geometry

Changes in geometry influence the theoretical spectra to a different degree, depending on the *syn*- and *anti*-ring type of isomerism. For the *anti* isomers the calculated electronic transitions are only to a small degree sensitive to a deviation from planarity of both moieties. In a case of an *exo*-bending, the wavelengths change no more than by 2 nm, also the changes of oscillator strengths are very limited. This is not so, however, for the *syn* isomers. A deviation from planarity by 5° and 9° causes the hypsochromic shifts with an average of 8 nm for naphthalenophane and 12 nm for anthracenophane. These changes are the greatest in the longwave region and the smallest in the shortwave region. They amount for naphthalenophane 18 and 2 nm, for anthracenophane 22 and 2 nm. The oscillator strengths decrease with increased bending, the changes being more pronounced for naphthalenophane.

Substituent and Pseudosubstituent Effects

Changes in the shortwave range of the experimental spectra (in which the bands for naphthalenophanes are denoted as β and β' and for anthracenophanes as β) correspond qualitatively to the changes which can be found in the spectra of *DMN* and DMA, respectively. This fact points to a specific pseudo-substituent effect originating from the deviation from planarity of the apex carbon atoms localized in the boat-shaped benzene rings.

The substituent effect resulting from the presence of methylene groups is reflected in the splitting and shifting of the theoretical bands. In the spectrum of *DMN* the band β at 207.5 nm and the band β' at 196.2 nm show a splitting into the pairs of bands at 217.0, 199.4 nm and 200.2 and 190.0 nm. Also, all bands show a bathochromic shift. For DNA the β band at 231.3 nm is split into the 249.0 and 226.8 nm bands. The bands shift bathochromically, except the β' band (Fig. 3).

In the cyclophanes under investigation the pseudo-substituent effect appears only in the shortwave region of the spectra. For naphtalenophanes the effect appears in the bands at 236.5, 180.8, and 177.8 nm (*syn*-ring) and 247.3, 191.2 nm (*anti*-ring); for anthracenophanes the bands appear at 248.9, 224.8 nm and 253.2, 240.6 nm. All the examples listed originate from a split of the β bands. The naphthalenophane bands at 236.5 and 247.3 nm corresponding to experimental bands at 245.5 (*syn*) and 239.0 nm (*anti*) result from a transannular effect. Obviously, this effect does not take place in *DMN*, the spectrum of which shows an absorptions minimum in the considered region. All these examples confirm the existance of a pseudo-substituent effect. In the calculations performed neither the π-electrons nor some special parameters were taken into consideration as it is usually done in case of a standard treatment aiming at an interpretation of the usual substituent effect of the methyl groups in *DMN* and *DMA*.

Transannular Effects

Napthalenophanes show a weak but still observable absorption in the region near 325 nm, which is interpreted as originating from the 301.7 nm band of naphtalene. This proves the presence of a transannular coupling in naphthalenophanes because the band corresponds to the transannular $b_{1g(\alpha)}$ band at 345.9 nm, typical for the spectrum of [2.2]paracyclophane[5]. Theoretical considerations and calculations point to the presence of two inactive maxima of absorption in the long-wave range of naphtalenophanes spectra, i.e. above 400 nm. The band for a *syn*-ring isomer shows a bathochromic shift with respect to that of the *anti*-ring isomer. We consider these bands as originated from the 277.6 nm band "p" of naphtalene. The same effect is observed for anthracenophanes. The longest wavelength bands originate from the p-type band of anthracene at 351.8 nm. Both the theoretical and experimental band of the *syn* isomer shows a bathochromic shift not found in the *anti* isomer. This bathochromic shift produces yellow coloration of the *syn* isomer. One can therefore assume that the bathochromic shift in the longwave region describes the extent of the transannular interaction in the phanes under consideration. Such interaction depends on the extent of overlapping of two chromophores and is greater for *syn*-ring isomers than for *anti*-ring isomers. Our calculations confirm this fact both for the case of naphthalenophanes and anthracenophanes. The transannular effect, stronger for the *syn*-ring isomers, is reflected in a split of naphthalene and anthracene bands (above 60 nm), being greater for the *syn* structures than for the *anti* structures. Accepting the extent of the split as a measure of transannular interactions, one can formulate the following order of decreasing interactions: *syn*-ring anthracenophane, *syn*-ring napthalenophane, *anti*-ring naphthalenophane and *anti*-ring anthracenophane.

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