Monatshefte für Chemie 112, 1175—1185 (1981)

Monatshefte für Chemie

Electronic Spectra of *syn*- and *anti*-Ring [2.2]Quinolinophanes

Leszek Czuchajowski*, **Antoni K. Wisor**, and **Maria J. Maślankiewicz**

Department of Organic Chemistry, Silesian University, 40007 Katowice, Poland

(Received 8 October 1980. Accepted 8 January 1981)

The energies and oscillator strengths of the singlet-singlet transitions for the *syn*- and *anti*-ring [2.2]quinolinophanes—regarded as quinoline dimers—were calculated using *PPP* CI-1 method and compared with experimental spectra. The theoretical transitions were assigned to the observed broad bands and characterised in terms of locally excited and charge transfer contributions. The influence of the pseudosubstituent effect is also discussed.

(Keywords: CT transitions; Electronic spectra; Isomeric [2.2]quinolinophanes; Local excitation transitions)

Elektronenspektrum von syn- und anti-Ring [2.2]Quinolinophanen

Die Anregungsenergie und Stärke des Oszillators vom Typ „singlet-singlet“ für *syn*- und *anti*-Ring [2.2]Quinolinophanen, betrachtet als Quinolinodimere, wurde mit dem Ultraviolett-Spektrum verglichen und nach der *PPP*-CI-1-Methode berechnet. Den beobachteten breiten Banden wurde die theoretische Übergangsenergie zugeordnet. Die Übergänge wurden nach ihrem Anteil an „lokalem Anregungscharakter“ (LE) und dem Ausmaß der Ladungsübertragung (CT) klassifiziert. Der Anteil des Pseudosubstituenteffekts wird diskutiert.

Introduction

The *anti*- and *syn*-ring [2.2]quinolinophanes synthesized recently in our laboratory[1,2] represent molecules, whose electronic spectra, considerably affected by transannular interaction, should be different for each isomer. Semiempirical Π-electron calculations of the transition energies in layer compounds, like some CT complexes and the phanes, bring about several difficulties because of the lack of a suitable parametrisation. However, the *PPP* CI-1 approach in the *Hinze-Beveridge* approximation[3] useful for spectroscopic problems, appeared promising in considering intramolecular interactions in the [2.2]para-

0026-9247/81/0112/1175/$ 02.20

cyclophane molecule. The chromophor in these molecules is regarded as a benzene dimer[4,5]. The fact that the investigated quinolinophanes can be considered both as derivatives of [2.2]paracyclophane and as quinoline dimers makes the present approach interesting.

The dimer-model of quinolinophanes suggests that a pure electronic treatment of the spectra of these systems may not be applicable because of the importance of vibronic coupling effects[6]. Fortunately enough, for all systems considered in this paper the so called strong coupling conditions are satisfied[6]. In the strong coupling limit the electron transition energies are only slightly affected by the coupling of electronic and nuclear motion and this validates the use of the *Born-Oppenheimer* approximation. Nevertheless the vibronic coupling effects will certainly influence the calculated band intensities. Thus, the intensity values that result from our calculations can undergo some changes due to the "intensity borrowing" coupling mechanism. This will lead to some enhancement of very weak and electronically forbidden bands[7].

Materials and Methods

The *anti*- and *syn*-ring [2.2]quinolinophanes were obtained according to authors' descriptions[1,2]. They were: dipyrido[4,5-b;15,16-b′] [2.2]paracyclophane (denoted subsequently as pseudo-*metha anti*-ring isomer, ps. *m.*), dipyrido[4,5-b;16,15-b′] [2.2]paracyclophane (pseudo-*para*, ps. *p.*), dipyrido[4,5-b;13,12-b′] [2.2]paracyclophane (pseudo-geminal *syn*-ring isomer, ps. *g.*) and dipyrido[4,5-b;12,13-b′] [2.2]paracyclophane (pseudo-*ortho*, ps. *o.*), see Fig. 1. The samples characterised by the following m..p's: 229-231 °C, 280-282 °C, 255-257 °C, and 229-231 °C respectively, used to produce the solutions in cyclohexane for the UV spectra recording, were additionally twice crystallized from chloroform-ethyl ether (1 : 1). The UV spectra were recorded on a Cary 118 spectrophotometer and on a Specord UV-VIS C. Zeiss instrument.

Satisfactory values of transition energies for quinoline and its formal structural units: benzene and pyridine, were achieved provided the resonance integral β_{kl} was calculated according to equ. (1)[3]:

$$\beta_{kl} = (1/2)\ (Z_k + Z_l)\ S_{kl}\ [\gamma_{kl} - (2\,C/r_{kl})] \qquad (1)$$

Therein S_{kl} is the overlap integral between atomic orbitals. In the calculation of S_{kl} the exponents $\zeta_C = 0.95718$ eV and $\zeta_N = 1.06124$ eV were used which fulfill the relation $\zeta_k = 0.086\,\gamma_{kk}$ eV. The value of the C parameter remained unchanged, $C = 0.545$. In the case of 5,8-dimethylquinoline, *DMQ*, for the two carbon atoms connected with the CH_3 groups, a value of $\omega = -10$ eV (instead of $\omega = -11.16$ eV) was used as a parameter for the ionisation potential[8]. The same values were taken into consideration for resonance integrals within the same quinoline structural moiety of quinolinophane. For interplanar resonance integrals some parameters were modified and taken as: $C' = 5.0\,C$, $\zeta_C = 1.625$ and for the $2\,p_\pi$ orbital of nitrogen—the value $\zeta_N = 1.95$.

The benzene rings in the four isomeric quinolinophanes were assumed to have boat conformation. It was assumed that the benzene—benzene structural fragment of every dimer represented the same geometry as in the [2.2]paracyclophane molecule[5]; the pyridine ring was assumed to be planar[9]. However, some geometry variations were introduced into each isomer so as to represent the whole molecule as a four membered ring system. Thereby several structures, (**a**) to (**h**) (presented in Fig. 1) were obtained.

The LCAO analysis proves that every MO of the dimer is characterised by a vector composed of two quinoline vectores in phase or in counter-phase

$$\mathbb{C}_j(+i) = \begin{pmatrix} \mathbb{C}_i^q \\ \mathbb{C}_i^q \end{pmatrix} \qquad \mathbb{C}_k(-i) = \begin{pmatrix} \mathbb{C}_i^q \\ -\mathbb{C}_i^q \end{pmatrix} \tag{2}$$

Therefore, every occupied and unoccupied MO of the monomer, i.e. of quinoline, in the dimer is represented by two MO's. Due to quasi degeneracy each single orbital excitation in the monomer splits into four orbital excitations in case of the dimer. From the point of view of the VB theory, these transitions can be regarded as occuring within the same monomer unit (locally excited transition, LE) or between the two monomer units (charge transfer transition, CT). The relevant characteristics is given by expressing the excited states of every quinolinophane molecule in terms of the LE and CT resonance structures.

Results

The electronic spectra of the two isomeric *syn*-ring quinolinophanes and the corresponding *anti*-ring isomers, together with the spectra of quinoline and 5,8-dimethylquinoline, are shown in Fig. 2. The absorption maxima and the oscillator strength values calculated for a given molecular structure are shown on each experimental spectrum, the corresponding wave length values being listed in Table 2 and 3, which present the pattern of splitting of theoretical quinoline energy levels. The calculations were performed for the four steric variants of every *syn*-ring and *anti*-ring isomer. The changes in geometry concerned the value of the angle of deviation of the plane of pyridine rings from coplanarity, and the interplanar distance, Fig. 1. Although all calculated

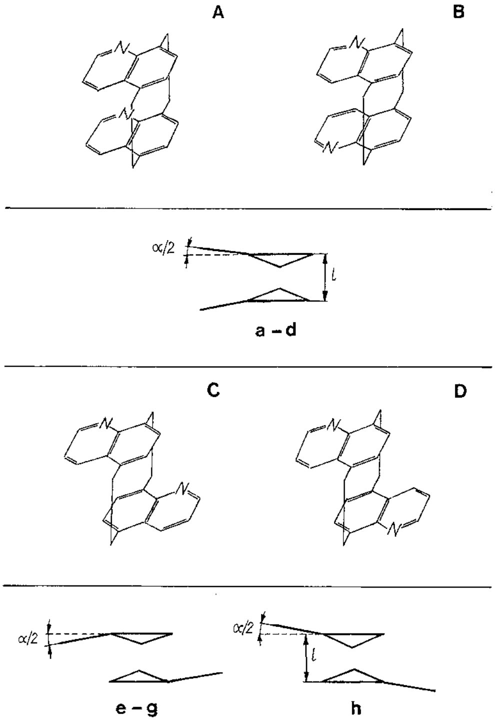

Fig. 1. The investigated isomers of [2.2]quinolinophanes: *A syn*-ring pseudo-geminal, *B syn*-ring pseudo-*ortho*, *C anti*-ring pseudo-*metha*, *D anti*-ring pseudo-*para*. The isomers A and B were considered in theoretical calculations in form of the structures **a** to **d**, the C and D isomers as **e** to **h**; **a**: $\alpha/2 = 0°$, $l = 3.09$ Å; **b**: $\alpha/2 = 2.5°$, $l = 3.09$ Å; **c**: $\alpha/2 = 5°$, $l = 3.09$ Å; **d**: $\alpha/2 = 2.5°$, $l = 3.11$ Å; **e**: $\alpha/2 = 0°$, $l = 3.09$ Å; **f**: $\alpha/2 = 0°$, $l = 3.11$ Å; **g**: $\alpha/2 = 5°$ *endo*, $l = 3.09$ Å; **h**: $\alpha/2 = 5°$ *exo*, $l = 3.09$ Å

values formed a basis for discussion, the values listed in Fig. 2 and Table 2 and 3 concern only the *syn*-ring isomers in which each pyridine ring forms an *exo* angle $\alpha/2 = 5°$ with the plane of the attached benzene unit, as it was found in [2.2]anthracenophanes[10]; the interplanar distance equals 3.11 Å. For the *anti*-ring isomers the structure with both moieties parallel and the same distance between the aromatic planes was considered.

Each theoretical maximum was characterised by the contribution of LE-CT transitions, Table 2 and 3, and in terms of the transitions in the quinoline molecule; the latter data are available from the authors on request. Electronic states of quinoline, see also [11], were compared—as a test of the adopted parametrisation—with those of benzene and pyridine, Table 1.

Table 1. *Characteristics of the singlet transitions of quinoline and the transitions in its structural units*

	Quinoline transition					Pyridine transition					Benzene transition				
No.	Energy, nm exp.[13]	Energy, nm calc.	Oscill. strength calc.	Type	Characteristics[a]	Type	Energy, nm exp.	Energy, nm calc.	Oscill. strength calc.	Type	Type	Energy, nm exp.	Energy, nm calc.	Oscill. strength calc.	Type
1	309	302.1	0.1951	α	60 (6,4), 33 (7,5), 2.7 (6,5)	$^1A_1$	200	206.1	0.1392	α	$^1B_{2u}$	254	252.3	0	α
2	281	279.1	0.3875	p	88 (6,5), 7 (7,4), 1.8 (6,4)	$^1B_2$	258	258.3	0.2946	p	$^1B_{1u}$	204	207.7	0	p
3	226	220.0	0.7982	β	34 (8,4), 28 (7,5), 15 (6,4)	$2\,^1A_1$	177	176.8	1.2053	β	$^1E_{1u}$	184	182.5	1.1745	β
4		214.9[b]	0.1550		86 (8,5), 10 (6,3), 1 (7,4)										
5	203	201.4	0.6990	β′	39 (7,4), 34 (6,3), 7 (7,5)										
6		199.2	1.0918		25 (7,5), 22 (8,4), 19 (7,4)										

[a] Participation of transitions between quinoline MO's.
[b] Unindexed within *Clar* notation.

Table 2. *Splitting of quinoline energy levels by the transannular interaction in the syn-ring isomers of [2.2]quinolinophane*

Quinoline transition, energy, nm		*syn*-ring pseudo-geminal isomer					*syn*-ring pseudo-*ortho* isomer				
exp.	calc.	Sym.	Energy, nm calc.	Oscillator strength calc.	No. in Fig. 2	LE/CT[a]	Sym.	Energy, nm calc.	Oscillator strength calc.	No. in Fig. 2	LE/CT
309	302.1 (α)	A''	382.3	0.045	2	41/57	B	376.3	0.056	2	41/58
		A''	305.6	0.055	4	53/44	A	303.6	0.158	4	45/55
		A'	301.9	0.159	5	45/52	B	301.5	0.071	5	52/46
		A'	207.5	0.883	14		A	205.9	0.826	14	
281	279.1 (p)	A''	478.7	0.001	1	56/42	A	463.1	0.006	1	56/42
		A'	311.4	0.328	3	55/40	B	316.0	0.322	3	55/42
		A'	235.0	0.235	9		B	232.4	0.162	10	36/59
		A''	192.1	0.054	17		A	197.8	0.026	15	
226	220.0 (β)	A'	230.0	0.835	10		B	239.9	0.149	8	30/50
		A'	190.1	0.511	18		A	189.3	0.254	18	
		A''	187.9	0.074	19		A	183.8	0.230	20	
		A''	181.4	0.017	21		B	188.2	0.115	19	

The short-wave quinoline theoretical bands (see Table 1) are splitted i.a. into the following levels: ps. g. isomer—279.1 (6), 244.2 (7), 239.2 (8), 225.5 (11), 225.2 (12), 197.5 (15), 196.6 (16); of *DMQ* origin—211.5 (13), 183.8 (20). Ps. *o*. isomer—274.2 (6), 242.1 (7), 232.5 (9), 225.8 (11), 220.7 (12), 197.5 (16), 195.2 (17); of *DMQ* origin—207.2 (13).

[a] Participation of the local excited and charge transfer transitions; the values are omitted when the contributions of LE and CT transitions are equal or almost equal.

Table 3. *Splitting of quinoline energy levels by transannular interaction in the anti-ring isomers of [2.2]quinolinophane*

Quinoline transition, energy, nm		*anti*-ring, pseudo-*metha* isomer					*anti*-ring, pseudo-*para* isomer				
exp.	calc.	Sym.	Energy, nm calc.	Oscillator strength calc.	No. in Fig. 2	LE/CT[a]	Sym.	Energy, nm calc.	Oscillator strength calc.	No. in Fig. 2	LE/CT
309	302.1 (α)	A	353.1	0.090	2	43/55	A_g	349.5	0	2	74/23
		B	307.4	0.293	4	26/62	A_u	305.9	0.285	4	89/7
		A	280.5	0.106	5	49/46	A_g	280.0	0	5	56/40
		B	206.5	0.481	13		A_u	208.7	0.498	13	
281	279.1 (p)	B	429.4	0.010	1	43/55	A_g	432.2	0	1	43/54
		A	322.9	0.284	3	42/57	A_u	323.2	0.314	3	38/59
		A	243.5	0.257	7	59/28	A_u	245.3	0.282	7	52/38
		B	214.6	0.331	12		A_g	212.4	0	12	
226	220.0 (β)	B	242.5	0.690	8	44/32	A_u	240.3	0.920	8	35/54
		A	222.1	0.025	11		A_g	222.1	0	11	
		A	186.4	0.484	17		A_g	187.7	0	17	
		B	183.7	0.508	18		A_u	183.4	0.477	18	

The short-wave quinoline theoretical bands (see Table 1) are splitted i.a. into the following levels: ps.*m*. isomer—262.4 (6), 236.6 (9), 223.7 (10), 196.8 (15), 193.2 (16); of *DMQ* origin—198.7 nm (14). Ps.*p*. isomer—262.1 (6), 238.9 (9), 223.3 (10), 195.9 (15), 193.6 (16): of *DMQ* origin—199.2 nm (14).

[a] Participation of local excited and charge transfer transitions; the values are omitted when the contributions of LE and CT transitions are equal or almost equal.

Discussion

The influence of geometry variation on theoretical spectra of quinolinophanes appeared different for the *anti*- and *syn*-ring isomers. In the case of the *anti*-ring structures the calculated transitions were very slightly sensitive to the deviation from co-planarity of both moieties. The wave length values usually changed within 1 nm, decreasing always for the *endo*-type bending, Fig. 1, **g**, and usually increasing for *exo*-bending, Fig. 1, **h**; the values of oscillator strength also showed limited changes. For the *syn*-ring isomers, the discussed changes were more distinct. The deviation from co-planarity, Fig. 1, **a** → **c**, caused a mean hypsochromic shift of ca. 7 nm for the pseudo-*ortho* isomer and of ca. 10 nm for the pseudo-geminal one, with higher changes (of the order of 30 nm) appearing for the two theoretical bands above 400 nm. Some substantial changes of oscillator strength were also noted. The increase of the interplanar distance, Fig. 1, **c** → **d**, led to a hypsochromic shift of ca. 19 and 8 nm of the two bands of the highest wave-length values, with the mean change of 4 nm for the whole spectral range. The oscillator strength did not change for the bands above 200 nm, and the differentiation between both *syn*-ring isomers was almost negligible. The changes in band intensities calculated for the ps. *m.*-ps. *p.*, i.e.both *anti*-ring isomers, as well as for the ps. g.-ps. *o.* (*syn*-ring) ones, particularly distinct in the 235–240 nm region, are obviously connected with the different typ of symmetry; the lack of real changes in transition energies is caused by isoelectronic character of the pairs of isomers considered.

Theoretical spectra of quinolinophanes, presented in Fig. 2 for the preferable form **d** of the *syn*-ring isomers and the **f** form of the *anti*-ring isomers, correspond quite well to the experimental spectra. Some differences between the *anti*- and *syn*-ring structures are apparent. This concerns both the experimental and the calculated spectra. The electronic structure of quinolinophanes is reflected by 30 calculated mono-excited singlet-singlet transitions. Twelve of them, originating from the splitting of quinoline α, β and p bands (in *Clar* notation), together with some additional transitions, are listed in Table 2 and 3. The changes in the experimental spectra of quinolinophanes concerning the short-wave region denoted as β′ band correspond qualitatively to the changes found by the authors in the 5,8-dimethylquinoline spectrum. This also indicates the presence of a specific pseudo-substituent effect connected with the deviations from planarity of apex carbon atom centers in benzene units. In the spectrum of *DMQ* the substituent effect, originating from the influence of methyl groups, results in a splitting of the two calculated short-wave quinoline bands,

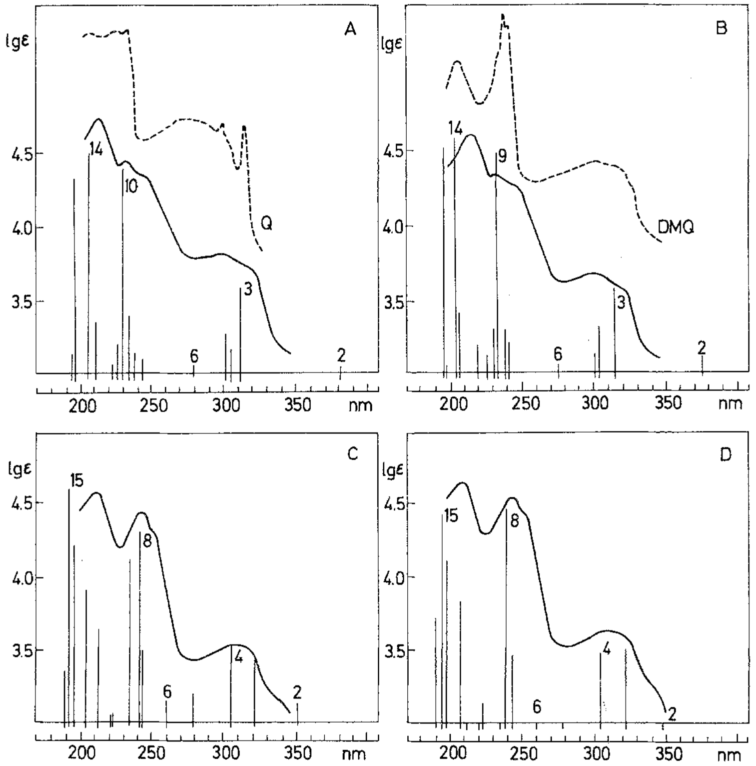

Fig. 2. Theoretical and experimental UV spectra (in cyclohexane) of the isomeric [2.2]quinolinophanes: *A syn*-ring pseudo-geminal, *B syn*-ring pseudo-*ortho*, *C anti*-ring pseudo-*metha*, *D anti*-ring pseudo-*para*. Theoretical bands are shown in a sequence from the band no. 2 toward the short-wave bands (band no. 1 is out of the presented range); the numbers of some bands are given as references to energy values in nm, listed in Table 2 and 3. Dotted lines show the experimental spectra of quinoline[13], *Q*, and 5,8-dimethylquinoline, *DMQ*

201.1 → 203.2, 182.0 nm (the 203.2 nm transition appears in the experimental spectrum at 205 nm); 199.2 → 192.9, 173.1 nm, and in a bathochromic shift of the remaining β, p and α bands, see Fig. 2. In quinolinophanes, the pseudo-substituent effect is limited only to the short-wave region. For instance, the theoretical bands at 199.2 nm in ps. p. (*anti*-ring) isomer spectrum and at 207.2 nm in the corresponding *syn*-ring structure, prove the existence of the mentioned effect, because contrary to the procedure applied in the interpretation of the usual substituent effect of methyl group, cf. *DMQ*, no additional Π-electrons and no additional parameters have been introduced in the course of the calculations.

Attention should also be paid to quinolinophanes absorption at ca. 340 nm, where the band is small but still observable. The appearance of this band, interpreted as originating from the 302.1 nm quinoline band, is a convincing proof of the existence of transannular coupling in quinolinophanes because it corresponds to the transannular $b_{1g}(\alpha)$ band at 345.9 nm, characteristic for the [2.2]paracyclophane spectrum[5].

Theoretical considerations and calculations also suggest the existence of the fifth absorption range above 400 nm, originating from quinoline transition at 279.1 (p) nm, its position for the *syn*-ring isomers showing a bathochromic shift with respect to that of the *anti*-ring isomers (the former ones are of pale-yellow colour). The character of this shift is similar to that shown by [2.2]anthracenophanes, for which the *syn*-ring isomer is coloured, contrary to the *anti*-ring compound[12]. Stronger transannular effect in *syn*-ring quinolinophanes than in the anti-ring ones is reflected by the split of the mentioned quinoline band into much wider (of about 60 nm) range of wave-length values for the *syn*-ring isomers.

Evaluation of local excitation and charge transfer character of transitions in quinolinophanes show that in most cases both types of transitions contribute to the spectrum to a similar extent, higher differences being noted for the *anti*-ring isomers. Although the four long-wave transitions show stronger CT character for one of the latter isomers (ps. *m.*) than the other bands, this does not seem to be a rule.

Acknowledgement

The authors are grateful to Dr. *S. A. Kucharski*, of the same laboratory, for helpful discussions. The research was sponsored by the Polish Academy of Sciences as a part of the MR-I-9 project.

References

[1] *Maślankiewicz M. J.*, *Czuchajowski L.*, Bull. Acad. Polon. Sci., ser. sci. chim. **27**, 167 (1979).

[2] Ibid. (in print).

[3] *Beveridge D. L.*, *Hinze J.*, J. Amer. Chem. Soc. **93**, 3107 (1971).

[4] *Iwata S.*, *Fuke K.*, *Sasaki M.*, *Nagakura S.*, *Otsubo T.*, *Misumi S.*, J. Mol. Spectr. **46**, 1 (1973).

[5] *Czuchajowski L.*, *Pietrzycki W.*, J. Mol. Struct. **47**, 423 (1978).

[6] *Witkowski A.*, in: Modern Quantum Chemistry, Istanbul Lectures, Vol. 3, p. 161. Academic Press. 1965.

[7] *McGlynn S. P.*, *Dougherty D.*, *Mathers T.*, *Abdulner S.*, Jerusalem Symp. Quantum Chem., Biochem., Vol. 10, 247 (1977).

[8] *Kwiatkowski J. S.*, private communication.

[9] Tables of Interatomic Distances and Configuration of Molecules and Ions, Chem. Soc. Special Publ. No. 18, p. 120. London. 1965.

[10] *Toyoda T.*, *Misumi S.*, Tetrahedron Lett. **1978**, 1479.

[11] *Nishimoto K.*, *Nakatsukasa K.*, *Fujishiro R.*, *Kato S.*, Theor. Chim. Acta **14**, 80 (1969).

[12] *Iwama A.*, *Toyoda T.*, *Yoshida M.*, *Otsubo T.*, *Sakata Y.*, *Misumi A.*, Bull. Chem. Soc. Japan **51**, 2988 (1978).

[13] UV Atlas of Organic Compounds (*DMS*), Vol. I. London: Butterworth; Weinheim: Verlag Chemie.