ELECTRONIC ABSORPTION, FLUORESCENCE AND POLARISATION SPECTRA OF β,β′-DIAMINO-9,10-ANTHRAQUINONES AND THEIR INTERPRETATION BY THE METHOD OF CONFIGURATION ANALYSIS*

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

On the basis of measurement of absorption frequency-dependent polarisation spectra of fluorescence (APF) and dichroism on oriented polyvinyl alcohol sheets, interpretation has been carried out of electronic absorption spectra of β,β′-diamino-9,10-anthraquinones in the wavelength range 250 to 600 nm. Character of the excited $\pi\pi^*$ states has been determined by the method of configuration analysis (PPP–CA).

Part X of this series[1] dealt with interpretation and characterization of $\pi\pi^*$ electronic transitions of 1- and 2-amino-9,10-anthraquinones on the basis of results of the PPP–CA method and with the use of polarisation spectra. The same experimental techniques and theoretical methods were used in Part XI (ref.[2]) for investigation of electronic spectra of α,α′-diamino-9,10-anthraquinones.

The aim of the present communication is interpretation of electronic spectra and investigation of character of the electronic $\pi\pi^*$ excited states of β,β′-diamino-9,10-anthraquinones with the use of the same experimental and theoretical methods as those used in the previous reports[1,2]. The theoretical $\pi\pi^*$ electronic spectra were obtained by the PPP method with the so called β-parameters ($b(\mathrm{C{=}O}) = 0{\cdot}7$; $b(\mathrm{C{-}NH_2}) = 0{\cdot}7$; for details see ref.[1]).

RESULTS AND DISCUSSION

Fig. 1 gives electronic spectrum of 2,3-diamino-9,10-anthraquinone; scheme *A*. This compound exhibits very weak fluorescence, which prevented measurement of its APF

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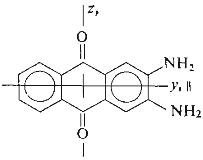
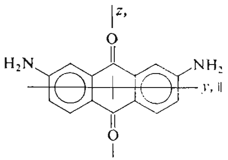
spectrum. Assignment of transitions to the experimental absorption spectrum was carried out on the basis of results of measurement of the polarisation spectra on oriented polyvinylalcohol sheets. With respect to molecular symmetry C_{2v}, the absorption spectrum could be analyzed with the help of the reduced spectra[2,3]. Interpretation of the spectrum follows from Fig. 1. The first absorption band is polarized perpendicularly to the axis of orientation; the region 2·3 to 3·3 μm^{-1} contains several bands with mutually parallel polarisation – parallel to the axis of orientation (a broad region with a high value of dichroism degree). The region of minimum of the absorption curve at 3·7 μm^{-1} corresponds to the minimum at the D curve, *i.e.* the region contains bands with perpendicular polarisation with respect to the axis of orientation. The region 4·0 μm^{-1} obviously contains overlapped bands with mutually opposite polarisation. Large overlap of bands in the whole region of UV spectrum (also observable from the reduced spectra) makes the assignments of other transitions doubtful.



A



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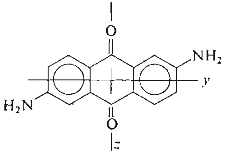


C

Fig. 2 gives absorption and polarisation spectra of 2,7-diamino-9,10-anthraquinone; scheme *B*. Identical course of APF and D curves indicates that the axis of orientation of this compound on polyvinyl alcohol sheet is identical with direction of polarisation of the first singlet $\pi\pi^*$ transition, *i.e.* with that of the *y* axis. Assignment of all the considered transitions on the basis of polarisation measurements is evident. Noteworthy is the local minimum of APF and D curves in the region 3·1 μm^{-1} indicating the presence of a band polarized perpendicularly to the axis of orientation (*y*). This band is present in the A'_y curve of the reduced spectrum, being, however, not observed in the absorption curve due to overlap with a very strong band with the maximum at 3·3 μm^{-1}. In the region 3·6 to 4·0 μm^{-1} the D curve exhibits a distinct minimum (the APF spectrum could not be measured in this region because of very low intensity of fluorescence), which indicates the presence of one or several bands polarized perpendicularly to the axis of orientation. These bands could correspond to two transitions of mutually parallel polarisation in the region 3·5 μm^{-1} of the theoretical spectrum.

Fig. 3 gives absorption spectrum of 2,6-diamino-9,10-anthraquinone; scheme *C*. As we failed to dye polyvinyl alcohol sheet with this substance and detect its luminescence, the information on band polarisation is missing. Therefore, spectrum of the compound cannot be interpreted in detail.

Table I gives the theoretical spectral characteristics of β,β'-diamino-9,10-anthraquinones.

Table II summarizes the results of configuration analysis. 2-Amino-9,10-anthraquinone was used as the reference system. In analogy to α,α'-diamino-9,10-anthra-

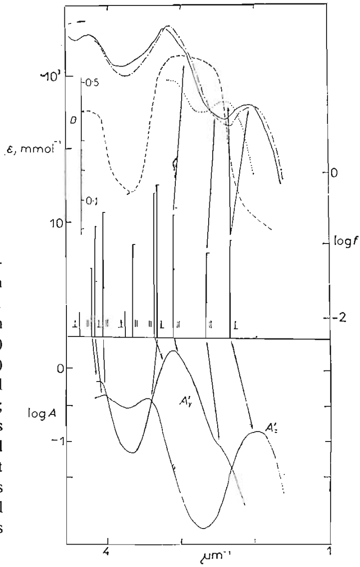


FIG. 1

Electronic spectrum of 2,3-diamino-9,10-anthraquinone; (———) the absorption spectrum in ethanol–methanol mixture 4 : 1 at 88 K; (–·–·–·) the absorption spectrum on oriented polyvinyl alcohol sheet; (·······) the absorption spectrum in benzene; (– – – – –) the dichroic curve on oriented polyvinyl alcohol sheet; D degree of dirchroism; A'_y, A'_z the reduced spectra; the vertical lines denote the theoretical transitions calculated by PPP method; the vertical lines without flat serif denote the theoretical transitions having log $f < -2$; assignment of individual transitions to the corresponding bands is denoted by arrows quinones, the most important finding is that of participation of the first excited state of the reference system in the first two excited states of β,β′-diamino-9,10-anthraquinones. The first excited state has a predominantly local character with a significant contribution of CT configuration, the second excited state has not so pronounced local character with similarly significant contribution of CT configuration. Thus in analogy to α,α′-diamino-9,10-anthraquinones, we can speak about "splitting" of the first transition of 2-amino-9,10-anthraquinone caused by introduction of the second amino group into β position. Table II shows besides the "mixed" states also further distinctly local states. Correlations between the states of the reference system and those of β,β′-diamino derivatives can be seen in Fig. 4. "Splitting" of the first transition is greater, if the both amino groups are at the same nucleus, being – on the contrary – smaller, if the amino groups are in different nuclei. As compared with the 1,4-isomer[2], the "splitting" of the 2,3-isomer is perceptibly smaller. Correlations of the transitions in shorter-wave region were carried out only in the cases

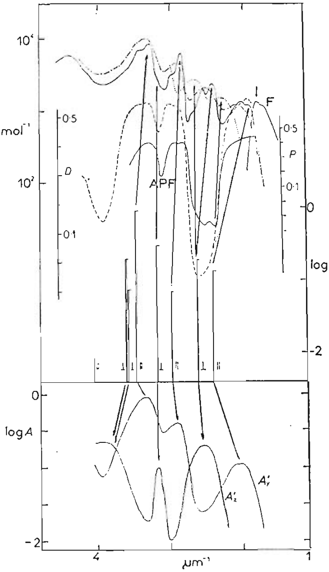


FIG. 2

Electronic spectrum of 2,7-diamino-9,10--anthraquinone; (———) the absorption spectrum in ethanol-methanol 4 : 1 at 88 K; (F—) the fluorescence spectrum in ethanol--methanol mixture 4 : 1 at 77 K (the small arrow denotes the wave number at which the excitation spectrum was measured); (APF—) the absorption frequency-dependent polarisation spectrum of fluorescence in ethanol-methanol mixture 4 : 1 at 77 K; (–·–·–·) the absorption spectrum in oriented polyvinyl alcohol sheet; (·······) the absorption spectrum in benzene; (------) the dichroic curve in oriented polyvinyl alcohol sheet; *D* degree of dichroism; *P* degree of fluorescence polarisation; A'_y, A'_z the reduced spectra; the vertical lines denote the theoretical transitions calculated by the PPP method, the vertical lines without flat serif denote the theoretical transitions having $\log f <$ < -2; assignment of individual transitions to the corresponding absorption bands is denoted by arrows

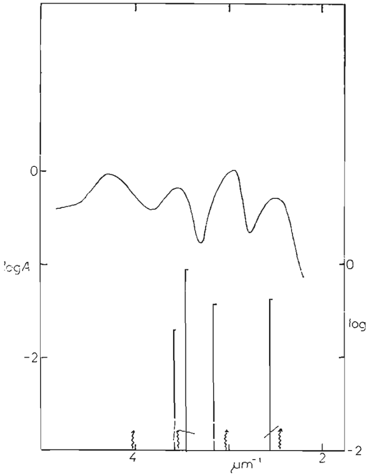


FIG. 3

Electronic spectrum of 2,6-diamino-9,10-anthraquinone; (———) the absorption spectrum in ethanol at room temperature; the vertical lines denote the theoretical transitions calculated by the PPP method, the short lines denote directions of the transition moments with respect to y-axis; ⟿ denote the forbidden transitions

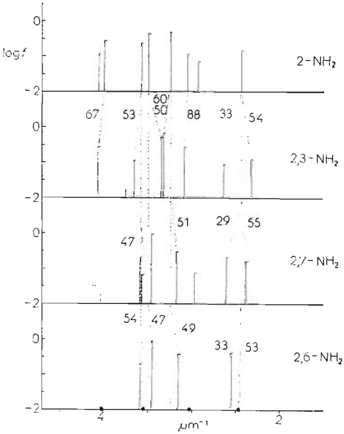
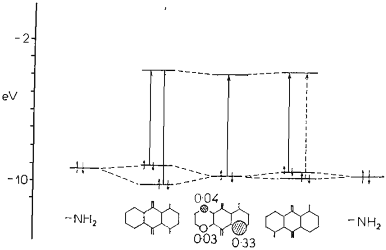


FIG. 4

The correlation graph of singlet excited states for β,β'-diamino-9,10-anthraquinones (and 2-amino-9,10-anthraquinone as the reference system) constructed on the basis of the PPP–CA results; full circle denotes the forbidden transitions; the vertical lines without flat serif denote the transitions having log $f <$ < -2

FIG. 5

The MO correlation graph representing the HOMO-HOMO interaction between 2-amino-9,10-anthraquinone and β-amino group



in which participation of the reference system exceeded 45%, and transition to this state had the value $\log f < -1$.

The character of $\pi\pi^*$ transitions determined from changes of the LCI π-electron charges[4] (fragmentation to 9,10-anthraquinone and two amino groups) is given in Table III for the first four transitions. It can be stated that the first two transitions of all three isomers have a pronounced CT character. The third and the fourth transitions are purely local transitions with the 2,3-isomer, being "mixtures" of the local and CT transitions with the 2,6- and 2,7-isomers.

Magnitude of the splitting of the first absorption band of 2-amino-9,10-anthraquinone caused by introduction of the second amino group into β position depends on position of the substitution, which can be explained on the basis of the MO correlation graph (Fig. 5). The interaction of $2p_\pi$ MO of nitrogen atom of NH_2 group with the HOMO of 2-amino-9,10-anthraquinone is great (large expansion coefficient), if the substituent is at 3 position, whereas for the 6- or 7-substitution it is small (small expansion coefficient). Magnitude of the splitting is also seen from the MO correlation graph representing interaction between four highest occupied MOs of 9,10-anthraquinone and two $2p_\pi$ MOs of nitrogen atoms of β-NH_2 groups expressed as their linear combinations (Fig. 6). In the case of the substitution at 2 and 3

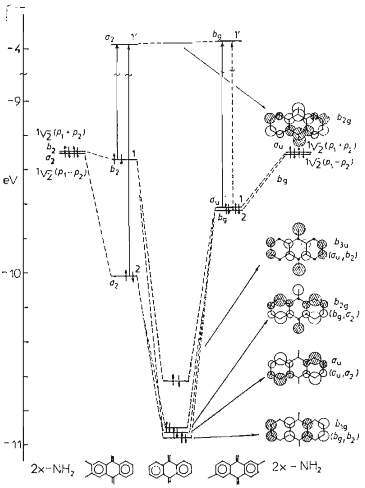


FIG. 6

The MO correlation graph of β,β'-diamino-9,10-anthraquinones using the fragmentation of 9,10-anthraquinone and two NH_2 groups positions a strong interaction takes place between symmetrical combination of $2p_\pi$ MOs of nitrogen atoms and the first and fourth occupied MOs of 9,10-anthraquinone (large expansion coefficients at 2 and 3 positions); the unsymmetrical combination

TABLE I

Theoretical spectral characteristics of the first eight singlet $\pi\pi^*$ transitions calculated by the PPP method with variable β^c and γ integrals and the parameters given in Table I of ref.[1]; the y-axis is perpendicular to connecting line of C=O bonds

n	Symmetry	$\Delta^1 E_n(S_0 \rightarrow S_n)$ eV	$\Delta^1 E_n(S_0 \rightarrow S_n)$ μm^{-1}	log f	$\sphericalangle$ (**M**, y)	The first two main configurations
			2,3-Diamino-9,10-anthraquinone			
1	B_2	2·875	2·320	−0·914	⊥	1,1′ (94·8)
2	A_1	3·274	2·642	−1·065	∥	2,1′ (77·8); 1,2′ (12·7)
3	A_1	3·828	3·089	−0·575	∥	4,1′ (87·3)
4	B_2	4·120	3·324	−0·165	⊥	3,1′ (92·5)
5	A_1	4·155	3·352	−0·280	∥	1,2′ (58·3); 2,1′ (20·3);
6	A_1	4·534	3·658	−0·957	∥	5,1′ (97·4)
7	B_2	4·647	3·749	−2·585	⊥	2,2′ (75·4); 2,4′ (17·4)
8	A_1	5·039	4·066	−0·556	∥	3,2′ (65·8); 1,4′ (12·7)
			2,6-Diamino-9,10-anthraquinone			
1	A_g	3·042	2·454	f	—	2,1′ (95·4)
2	B_u	3·166	2·555	−0·368	220°	1,1′ (82·0)
3	A_g	3·751	3·026	f	—	4,1′ (69·7); 1,2′ (20·0)
4	B_u	3·914	3·158	−0·423	94°	3,1′ (43·9); 5,1′ (17·8)
5	B_u	4·283	3·455	−0·054	349°	2,2′ (59·3); 3,1′ (19·3)
6	A_g	4·404	3·553	f	—	1,2′ (55·4); 4,1′ (28·7)
7	B_u	4·447	3·588	−0·699	88°	5,1′ (66·7); 3,1′ (22·3)
8	A_g	4·993	4·028	f	—	1,3′ (60·5); 3,2′ (21·1)
			2,7-Diamino-9,10-anthraquinone			
1	B_2	2·967	2·394	−0·872	∥	1,1′ (95·6)
2	A_1	3·237	2·612	−0·698	⊥	2,1′ (84·6)
3	B_2	3·687	2·975	−1·131	∥	4,1′ (78·8); 1,2′ (12·9)
4	A_1	3·934	3·174	−0·515	⊥	3,1′ (46·1); 2,2′ (17·9)
5	B_2	4·292	3·463	−0·039	∥	1,2′ (63·6); 4,1′ (19·0)
6	A_1	4·421	3·567	−1·177	⊥	5,1′ (73·9); 2,2′ (13·0)
7	A_1	4·444	3·585	−0·702	⊥	3,2′ (43·4); 2,2′ (40·1)
8	B_2	5·003	4·037	−2·497	∥	2,3′ (59·7); 4,2′ (16·2)

interacts with the second and third occupied MOs of 9,10-anthraquinone, and this interaction is small due to small expansion coefficients at 2 and 3 positions in these

TABLE II

Results of configuration analysis (PPP–CA) for β,β′-diamino-9,10-anthraquinones using 2-amino-9,10-anthraquinone as the reference system (the S_n^0 excited states), NB means non-bonding configuration of the ground state of the system (2-amino-9,10-anthraquinone + NH_2 group); r_M is the index expressing suitability of the chosen fragmentation ($r_M \leqq 100\%$)

$\tilde{\nu}$, μm^{-1}	log f		% NB	S_1^0	S_2^0	S_3^0	S_4^0	S_5^0	S_6^0	S_7^0	S_8^0	% CT	% r_M
		2,3-Diamino-9,10-anthraquinone											
—	—	S_0	91	0	0	0	0	0	0	0	0	7	99
2·320	−0·914	S_1	1	54	10	0	0	0	0	0	0	25	92
2·642	−1·065	S_2	0	33	30	1	1	0	0	0	0	27	92
3·089	−0·575	S_3	0	0	2	88	1	0	0	0	0	1	92
3·324	−0·165	S_4	0	1	22	2	60	0	0	0	0	7	92
3·352	−0·280	S_5	1	2	1	0	3	50	1	1	2	27	92
3·658	−0·957	S_6	0	0	7	0	10	6	53	0	0	14	91
3·749	−2·585	S_7	1	0	2	0	2	16	0	12	21	26	91
4·066	−0·556	S_8	0	0	0	0	0	0	0	67	23	1	91
		2,7-Diamino-9,10-anthraquinone											
—	—	S_0	91	0	0	0	0	0	0	0	0	7	98
2·394	−0·872	S_1	1	55	0	4	1	0	1	0	0	28	91
2·612	−0·698	S_2	0	29	7	23	6	0	0	0	0	25	91
2·975	−1·131	S_3	0	0	71	13	0	0	1	0	0	5	91
3·174	−0·515	S_4	0	1	6	22	51	0	0	0	0	15	91
3·463	−0·039	S_5	1	0	1	4	3	43	2	8	4	23	91
3·567	−1·177	S_6	1	0	1	6	8	10	47	1	0	14	90
3·585	−0·702	S_7	0	0	0	5	0	36	8	17	6	15	91
4·037	−2·497	S_8	0	0	0	0	0	0	1	5	46	19	91
		2,6-Diamino-9,10-anthraquinone											
—	—	S_0	91	0	0	3	0	0	0	0	0	8	99
2·454	f	S_1	1	53	3	7	1	0	1	0	0	28	91
2·555	−0·368	S_2	1	33	20	49	6	0	0	0	0	24	91
3·026	f	S_3	0	0	32	13	2	0	1	0	0	7	91
3·158	−0·423	S_4	0	0	17	6	49	0	0	0	0	10	91
3·455	−0·054	S_5	1	0	0	3	1	47	0	8	4	21	91
3·553	f	S_6	0	0	0	5	1	40	2	16	7	17	91
3·588	−0·699	S_7	0	0	3	0	8	2	54	0	0	14	89
4·028	f	S_8	1	0	0	0	0	0	1	37	13	19	91

TABLE III

The character of transitions of β,β′-diamino-9,10-anthraquinones determined from changes of the LCI π-electron charges at the subsystems during $S_0 \rightarrow S_n$ transition; 9,10-anthraquinone and two amino groups are considered as the subsystems

Transition	Character	%	Transition type	Δq_S[a]	Δq_{CT}[b]	Δq_{LE}[c]
			2,3-Diamino-9,10-anthraquinone			
$S_0 \rightarrow S_1$	CT	89	2,3-$NH_2 \rightarrow$9,10-AQ		0·64	—
	LE	11	9,10-AQ	0·72	—	0·08
$S_0 \rightarrow S_2$	CT	87	2,3-$NH_2 \rightarrow$9,10-AQ		0·56	—
	LE	13	9,10-AQ	0·65	—	0·08
$S_0 \rightarrow S_3$	CT	4	2,3-$NH_2 \rightarrow$9,10-AQ		0·02	—
	LE	96	9,10-AQ	0·48	—	0·46
$S_0 \rightarrow S_4$	CT	—	2,3-$NH_2 \rightarrow$9,10-AQ			—
	LE	100	9,10-AQ	0·43	—	0·43
			2,6-Diamino-9,10-anthraquinone			
$S_0 \rightarrow S_1$	CT	87	2,6-$NH_2 \rightarrow$9,10-AQ		0·58	—
	LE	13	9,10-AQ	0·67	—	0·09
$S_0 \rightarrow S_2$	CT	74	2,6-$NH_2 \rightarrow$9,10-AQ		0·50	—
	LE	26	9,10-AQ	0·68	—	0·18
$S_0 \rightarrow S_3$	CT	29	2,6-$NH_2 \rightarrow$9,10-AQ		0·12	—
	LE	71	9,10-AQ	0·42	—	0·30
$S_0 \rightarrow S_4$	CT	41	2,6-$NH_2 \rightarrow$9,10-AQ		0·20	—
	LE	59	9,10-AQ	0·49	—	0·29
			2,7-Diamino-9,10-anthraquinone			
$S_0 \rightarrow S_1$	CT	90	2,7-$NH_2 \rightarrow$9,10-AQ		0·59	—
	LE	10	9,10-AQ	0·65	—	0·07
$S_0 \rightarrow S_2$	CT	91	2,7-$NH_2 \rightarrow$9,10-AQ		0·54	—
	LE	9	9,10-AQ	0·59	—	0·05
$S_0 \rightarrow S_3$	CT	15	2,7-$NH_2 \rightarrow$9,10-AQ		0·09	—
	LE	85	9,10-AQ	0·62	—	0·52
$S_0 \rightarrow S_4$	CT	39	2,7-$NH_2 \rightarrow$9,10-AQ		0·19	—
	LE	61	9,10-AQ	0·48	—	0·29

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[a] The total redistribution of π-electron charge (CT migration + LE redistribution); [b] the migration of the total amount of π-electron charge during CT transition; [c] the redistribution of the total amount of π-electron charge during LE.

two MOs. This fact results in relatively large splitting of the first two occupied MOs of 2,3-diamino-9,10-anthraquinone. In the case of the 2,6- and 2,7-disubstitutions the symmetrical combination interacts with the first and third (and the unsymmetrical one with the second and fourth) occupied MOs of 9,10-anthraquinone. The both interactions are of comparable magnitude because of magnitude of expansion coefficients of the first four occupied MOs of 9,10-anthraquinone at 6 and 7 positions; consequently, the splitting of the first two occupied MOs of 2,6- and 2,7-diamino-9,10-anthraquinone is only very small. From the above discussion it is also obvious why the splitting of the first two occupied MOs is greater with 1,4-diamino-9,10-anthraquinone[2] than with 2,3-isomer.

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