ELECTRONIC ABSORPTION, FLUORESCENCE, AND POLARISATION SPECTRA OF α,α′-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 absorption spectra of α,α′-diamino-9,10-anthraquinones in the wavelength range 250 to 600 nm. Character of the excited states has been determined by the method of configuration analysis (PPP–CA).

The previous communication[1] of this series dealt with interpretation of electronic absorption spectra of 1- and 2-amino-9,10-anthraquinones on the basis of the PPP method in the approximation of quasireal geometry (variable β^c and γ integrals) with the help of APF spectra and measurement of dichroism on oriented polyvinyl alcohol sheets. Character of the excited states was determined by the method of configuration analysis and discussed in terms of locally excited (LE) states in the subsystems and charge-transfer (CT) states between the subsystems. The above-mentioned communication also gives a survey of papers dealing with interpretation of electronic spectra of 9,10-anthraquinone derivatives.

This communication gives interpretation of electronic spectra and studies character of the excited states of α,α′-diamino-9,10-anthraquinones using the same experimental and theoretical methods as in the previous paper[1]. In the case of the systems belonging to C_{2v} symmetry point group it was also possible to assign transitions to absorption bands on the basis of so called reduced curves.

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EXPERIMENTAL

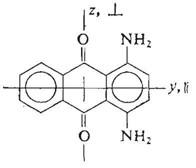
The substances investigated were prepared and purified in Research Institute of Organic Syntheses; their purity was checked by chromatography and by excitation fluorescence spectra.

The methods of measurement of absorption, fluorescence and dichroic spectra are described in the previous communication[1]. The so called normalized reduced curves[2] A'_y, A'_z (Figs 1, 2) are given for the molecules having C_{2v} symmetry, *i.e.* 1,4- and 1,8-diamino-9,10-anthraquinones. The *x*–*y*–*z* coordinate system is oriented with respect to the molecule in the following way: the *x*-axis is perpendicular to the plane of the molecule, the *y*-axis is in the molecular plane and perpendicular to the connecting line of C=O bonds, and the *z*-axis is perpendicular to *x*-axis and *y*-axis. The symbols A'_y and A'_z denote the spectra due to transitions with the moments oriented in the direction of *y*-axis and *z*-axis, respectively.

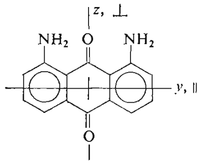
The theoretical $\pi\pi^*$ electronic spectra were obtained by the PPP method with the so called α-parameters (b(C=O) = 0·8; b(C—NH_2) = 0·7; for details see ref.[1]).

RESULTS AND DISCUSSION

Fig. 1 gives the absorption, fluorescence, and APF spectra along with the theoretical electronic spectrum and the reduced curves for 1,4-diamino-9,10-anthraquinone (scheme *A*); (C_{2v} symmetry point group, C_2 being identical with the *y*-axis). On the basis of the course of APF curve assignment of some transitions is possible (Fig. 1). Fairly unambiguous assignments to the individual spectral bands are those of the first (polarisation in the direction of *y*-axis), the second (*z*), the fourth (*y*) transitions (oscillations at the APF curve towards positive values in the region 3·0 to 3·5 μm^{-1}), the seventh (*z*) transition (a marked minimum at the APF curve) and the eight (*y*) transition. However, a more precise interpretation is possible on the basis of the reduced curves (Fig. 1).



A



B

Fig. 2 gives the spectral curves along with the theoretical transitions for 1,8-diamino-9,10-anthraquinone (scheme *B*); (C_{2v} symmetry point group, C_2 being identical with the *z*-axis). From the unsymmetrical shape of the first absorption band and, first of all, from the break of the APF curve at 2·2 μm^{-1} it is obvious that in the region 1·8 to

2·8 μm^{-1} there are two bands with mutually perpendicular polarisation. The break at the APF curve towards higher values of polarisation degree at 3·0 μm^{-1} indicates the presence of a further absorption band having polarisation parallel to the first absorption band. The marked minimum ($P \doteq -0{\cdot}2$) at the APF curve in the region of 3·5 μm^{-1} indicates another band with perpendicular polarisation to the first band (the PPP method predicts in this region three transitions with mutually parallel polarisation and relatively high probability of transition). Again the reduced curves (Fig. 2) enable a more precise and more detailed interpretation.

Fig. 3 gives the spectral curves and the theoretical electronic spectrum for 1,5-diamino-9,10-anthraquinone; scheme *C*. The APF curve has a clean-cut shape with the values of polarisation degree close to theoretical limits of polarisation degree of photoselection, *i.e.* $-0{\cdot}3 \leqq P \leqq +0{\cdot}5$. This result can be ascribed to the fact that, in spite of low symmetry of the molecule, the directions of transition moments are approximate-

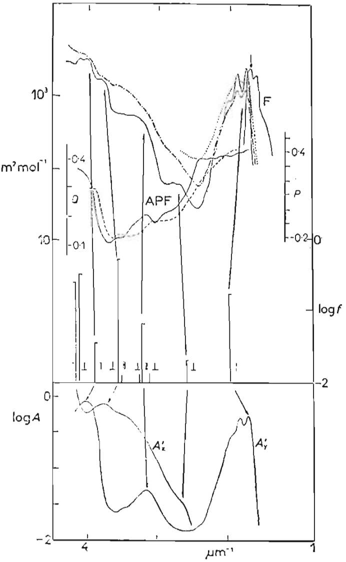
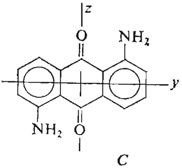


FIG. 1

Electronic spectrum of 1,4-diamino-9,10-anthraquinone; (———) absorption spectrum in ethanol–methanol mixture 4 : 1 at 88 K; (F—) 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—) absorption frequency-dependent polarisation spectrum of fluorescence in ethanol–methanol mixture 4 : 1 at 77 K; (–·–·–·) absorption spectrum on oriented polyvinyl alcohol sheet; (·······) absorption spectrum in benzene; (-----) dichroic curve on oriented polyvinyl alcohol sheet; *D* degree of dichroism; *P* degree of polarisation of fluorescence; A'_y, A'_z denote 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 the individual transitions to the corresponding absorption bands is denoted by arrows



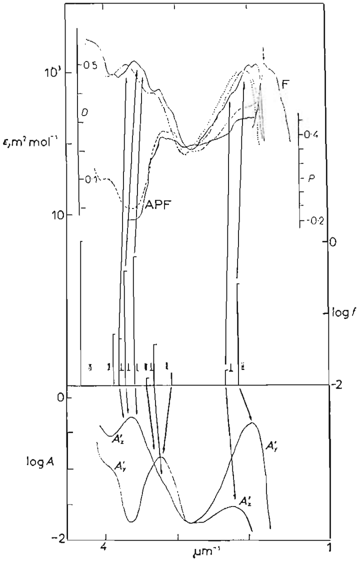


FIG. 2

Electronic spectrum of 1,8-diamino-9,10-anthraquinone (for explanation of symbols see Fig. 1)

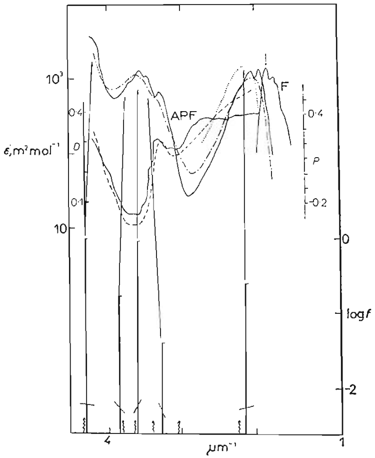


FIG. 3

Electronic spectrum of 1,5-diamino-9,10-anthraquinone (for explanation of symbols see Fig. 1); the short lines denote directions of the transition moments with respect to y-axis; ⁓⁓→ denote the forbidden transitions ly either mutually parallel or perpendicular. Due to the symmetry (C_{2h}) of the molecule, the theoretical $\pi\pi^*$ spectrum also involves symmetry-forbidden transitions. In the region 1·8 to 2·8 μm^{-1} the APF curve has a practically constant value of polari-

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 with the parameters given in Table I of ref.[1]; y-axis is perpendicular to connecting line of C=O bonds

n	Symmetry	$\Delta^1 E_n(S_0 \rightarrow S_n)$		log f	∢ (**M**, y)	The first two main configurations
		eV	μm^{-1}			
		1,4-Diamino-9,10-anthraquinone				
1	A_1	2·409	1·943	−0·675	‖	1,1′ (95·7)
2	B_2	3·153	2·544	−1·586	⊥	2,1′ (82·4); 1,2′ (9·4)
3	B_2	3·830	3·090	−3·161	⊥	5,1′ (66·8); 1,2′ (13·2)
4	A_1	3·933	3·173	−1·077	‖	4,1′ (83·2)
5	A_1	3·977	3·209	−3·539	⊥	1,2′ (51·0); 5,1′ (25·1)
6	A_1	4·323	3·487	−2·905	‖	1,3′ (62·6); 2,2′ (12·2)
7	B_2	4·335	3·498	−0·136	⊥	3,1′ (81·4); 1,2′ (14·7)
8	A_1	4·768	3·847	−1·334	‖	2,2′ (59·2); 1,3′ (19·5)
		1,5-Diamino-9,10-anthraquinone				
1	B_u	2·648	2·136	−0·586	192°	1,1′ (94·7)
2	A_g	2·774	2·238	f	—	2,1′ (91·4)
3	A_g	3·786	3·054	f	—	4,1′ (84·4)
4	B_u	4·082	3·293	−1·405	100°	2,2′ (45·0); 3,1′ (37·2)
5	A_g	4·222	3·406	f	—	1,2′ (64·7); 4,1′ (12·0)
6	B_u	4·469	3·605	−0·043	82°	3,1′ (57·4); 2,2′ (30·3)
7	A_g	4·524	3·650	f	—	5,1′ (72·1); 3,2′ (8·4)
8	A_g	4·708	3·799	f	—	1,3′ (60·4); 5,1′ (14·9)
		1,8-Diamino-9,10-anthraquinone				
1	B_2	2·612	2·107	−0·631	‖	1,1′ (93·8)
2	A_1	2·838	2·289	−1·862	⊥	2,1′ (93·2)
3	B_2	3·790	3·058	−2·321	‖	4,1′ (87·5)
4	A_1	4·076	3·289	−1·464	⊥	2,2′ (41·8); 3,1′ (35·3)
5	B_2	4·211	3·398	−1·945	‖	1,2′ (74·3); 4,1′ (10·2)
6	A_1	4·426	3·571	−0·242	⊥	3,1′ (43·4); 5,1′ (26·6)
7	A_1	4·577	3·693	−0·445	⊥	5,1′ (50·0); 2,2′ (23·8)
8	A_1	4·698	3·792	−1·363	⊥	1,3′ (60·8); 5,1′ (12·8)

sation degree, which indicates the presence of a single absorption band in this region – in accordance with theoretical prediction. From the wave number $2{\cdot}8\ \mu m^{-1}$ the APF and the D curves have decreasing character down to a deep minimum at $3{\cdot}6\ \mu m^{-1}$, which is due to several transitions in the region 3·2 to $3{\cdot}8\ \mu m^{-1}$ all of which have mutually nearly parallel polarisation and nearly perpendicular polarisation to the first band. The decrease of the APF and the D curves is interrupted by a local maximum at $3{\cdot}3\ \mu m^{-1}$ which indicates a band with more parallel polarisation to the first absorption band. This band appears as a shoulder in the absorption curve. However, the theoretical spectrum calculated for the molecule of C_{2h} symmetry does not involve any equivalent of this band. It can only be presumed that the band corresponds to some of the forbidden transitions, which is allowed by vibronic interaction.

Thus it can be stated that the theoretical predictions obtained by the PPP method agree very well with experimental results for all the systems discussed.

Table I gives the theoretical spectral characteristics of the first eight $\pi\pi^*$ electronic ransitions for the systems studied. The determination of characters of S_n $(\pi\pi^*)$ states has been carried out by the method of configuration analysis (PPP–CA) with 1-amino-9,10-anthraquinone as the reference system which means that the character of the

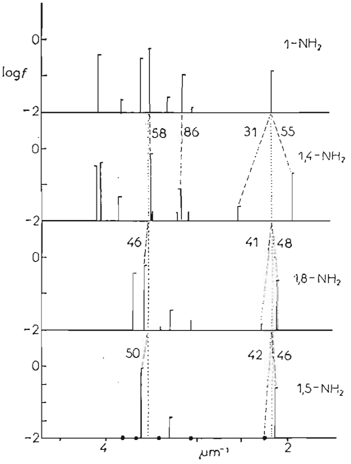


FIG. 4

The correlation graph of singlet excited states constructed on the basis of the PPP–CA results for α,α′-diamino-9,10-anthraquinones with 1-amino-9,10-anthraquinone as the reference system; full circle denotes the forbidden transitions, the vertical lines without flat serif denote the transitions having $\log f < -2$

states will be discussed in terms of local excitation (LE) in 1-amino-9,10-anthraquinone and CT excitation from the second amino group to 1-amino-9,10-anthra-

TABLE II

The results of configuration analysis (PPP–CA); the reference system is 1-amino-9,10-anthraquinone (excited states S_n^0), NB denotes non-bonding configuration of the ground state of the system (1-amino-9,10-anthraquinone + NH_2 group); r_M is the index expressing suitability of the fragmentation chosen ($r_M \leqq 100\%$)

$\tilde{\nu}$, 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
1,4-Diamino-9,10-anthraquinone													
—	—	S_0	88	0	0	0	0	0	0	0	0	9	98
1·943	−0·675	S_1	2	55	1	0	0	1	2	1	0	28	89
2·544	−1·586	S_2	2	31	12	0	2	1	4	1	0	33	89
3·090	−3·161	S_3	0	2	64	1	0	2	7	0	0	13	90
3·173	−1·077	S_4	0	0	1	86	1	0	0	0	0	0	89
3·209	−3·539	S_5	1	0	7	1	52	0	5	0	0	18	90
3·487	−2·905	S_6	0	0	1	0	11	7	0	41	0	27	90
3·498	−0·136	S_7	0	0	0	0	6	58	16	0	0	6	89
3·847	−1·334	S_8	2	0	1	0	14	3	6	11	1	29	90
1,8-Diamino-9,10-anthraquinone													
—	—	S_0	88	0	0	0	0	0	0	0	0	9	98
2·107	−0·631	S_1	1	48	0	12	0	0	0	0	0	28	90
2·289	−1·862	S_2	0	41	0	17	0	0	0	0	0	30	90
3·058	−2·321	S_3	0	0	84	0	1	0	0	0	0	3	90
3·289	−1·464	S_4	2	0	2	2	57	6	1	0	0	15	89
3·398	−1·945	S_5	2	0	1	2	29	8	7	0	1	24	89
3·571	−0·242	S_6	0	0	0	9	0	62	0	1	2	11	89
3·693	−0·445	S_7	0	0	0	14	0	1	46	0	0	18	89
3·791	−1·363	S_8	0	0	0	2	0	1	0	49	11	20	89
1,5-Diamino-9,10-anthraquinone													
—	—	S_0	88	0	0	0	0	0	0	0	0	9	98
2·136	−0·586	S_1	1	46	1	11	0	0	0	0	0	29	89
2·238	f	S_2	1	42	2	13	0	0	0	0	0	30	89
3·054	f	S_3	0	0	78	8	0	0	0	0	0	3	89
3·293	−1·405	S_4	1	0	3	1	52	10	0	0	1	2	89
3·406	f	S_5	2	0	2	1	34	11	2	0	1	23	89
3·605	−0·043	S_6	1	0	0	1	0	50	14	1	4	12	89
3·650	f	S_7	0	0	1	21	0	9	32	1	0	19	88
3·799	f	S_8	0	0	1	2	0	0	1	52	11	19	89

quinone. Thus we will be interested in the effect of introduction of the second α-amino group on the absorption spectrum of the reference system.

Table II gives the results of the configuration analysis. The most important finding is that the first excited state of the reference system contributes to the both first excited states of the discussed diamino-9,10-anthraquinones, hence we can speak about "splitting" of the first transition of 1-amino-9,10-anthraquinone by introduction of the second amino group into α position, even though contribution of CT configuration to the both first cited states cannot be ingored. Magnitude of the "splitting" of the first band and its manifestation in spectrum depended on the position into which the second amino group was introduced. Furthermore, Table II shows not only the existence of other "mixed" excited states but also the existence of states having predominant character of some of the states of the reference system, which means that the electronic $\pi\pi^*$ transition to these states is *de facto* the transition of 1-amino-9,10-anthraquinone.

The characters of $\pi\pi^*$ transitions determined from changes of LCI π-electron charges[3] (when using the fragmentation to 9,10-anthraquinone and two amino groups) are given in Table III for the first four transitions. For all the three isomers the first transition has a predominant character of CT transition with perceptible contribution of local transition (LE). The second transition has a pronounced character of CT transition. Character of the third and the fourth transitions depends on whether the both α-amino groups are located at the same nucleus (1,4-isomer) or at different nuclei (1,5- and 1,8-isomers). For the 1,4-isomer the third transition represents a "mixture" of local and CT transitions (with predominance of the former) and the fourth transition has a pronounced local character. For the 1,5- and 1,8-isomers the third transition has a predominant local character, and the fourth transition is a "mixture" of local and CT transitions (with predominance of the latter).

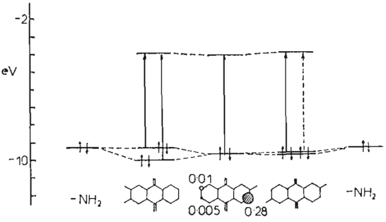


FIG. 5

The MO correlation graph representing the HOMO–HOMO interaction between 1-amino-9,10-anthraquinone and the second α-NH_2 group

TABLE III

The character of transitions of aminoanthraquinones determined from changes of LCI π-electron charges in subsystems during $S_0 \rightarrow S_n$ transition; α-NH_2 groups and 9,10-anthraquinone are considered to be the subsystems

Transition	Character	%	Transition type	Δq_S[a]	Δq_{CT}[b]	Δq_{LE}[c]
1,4-Diamino-9,10-anthraquinone						
$S_0 \rightarrow S_1$	CT	87	1,4-$NH_2 \rightarrow$9,10-AQ		0·59	—
	LE	13	9,10-AQ	0·67	—	0·08
$S_0 \rightarrow S_2$	CT	96	1,4-$NH_2 \rightarrow$9,10-AQ		0·74	—
	LE	4	9,10-AQ	0·77	—	0·03
$S_0 \rightarrow S_3$	CT	37	1,4-$NH_2 \rightarrow$9,10-AQ		0·23	—
	LE	63	9,10-AQ	0·62	—	0·39
$S_0 \rightarrow S_4$	CT	3	9,10-AQ$\rightarrow$1,4-NH_2		0·01	—
	LE	97	9,10-AQ	0·45	—	0·44
1,5-Diamino-9,10-anthraquinone						
$S_0 \rightarrow S_1$	CT	87	1,5-$NH_2 \rightarrow$9,10-AQ		0·60	—
	LE	13	9,10-AQ	0·68	—	0·09
$S_0 \rightarrow S_2$	CT	91	1,5-$NH_2 \rightarrow$9,10-AQ		0·64	—
	LE	9	9,10-AQ	0·70	—	0·07
$S_0 \rightarrow S_3$	CT	7	1,5-$NH_2 \rightarrow$9,10-AQ		0·04	—
	LE	93	9,10-AQ	0·63	—	0·58
$S_0 \rightarrow S_4$	CT	75	1,5-$NH_2 \rightarrow$9,10-AQ		0·36	—
	LE	25	9,10-AQ	0·48	—	0·12
1,8-Diamino-9,10-anthracquinone						
$S_0 \rightarrow S_1$	CT	82	1,8-$NH_2 \rightarrow$9,10-AQ		0·59	—
	LE	18	9,10-AQ	0·72	—	0·13
$S_0 \rightarrow S_2$	CT	91	1,8 - $NH_2 \rightarrow$9,10-AQ		0·63	—
	LE	9	9,10-AQ	0·69	—	0·06
$S_0 \rightarrow S_3$	CT	8	1,8-$NH_2 \rightarrow$9,10-AQ		0·06	—
	LE	92	9,10-AQ	0·66	—	0·61
$S_0 \rightarrow S_4$	CT	74	1,8-$NH_2 \rightarrow$9,10-AQ		0·34	—
	LE	26	9,10-AQ	0·46	—	0·12

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

The correlations obtained from the configurational analysis for α,α'-diamino-9,10-anthraquinones are given in Fig. 4. Introduction of the second amino group in the α position of the same nucleus causes large "splitting" of the first transition of 1-amino-9,10-anthraquinone, whereas its introduction in the α position of the other nucleus causes only small splitting; furthermore, for the 1,5-diamino derivative (C_{2h}) the second transition is symmetry-forbidden. The other transitions in the graph were connected only in those cases in which contribution of the reference configuration exceeded 50% and the respective transition had the value $\log f > -1$.

The MO correlation graph in Fig. 5 gives a clear explanation of magnitude of the "splitting" of the first absorption band of 1-amino-9,10-anthraquinone caused by introduction of the second α-amino group and its dependence on position of the substitution. Interaction between $2p_\pi$ MO of nitrogen atom of the second α-NH_2 group and the HOMO of 1-amino-9,10-anthraquinone is large, if the substituent is in 4 position (a large expansion coefficient), whereas it is small (small expansion coefficient), if the substituent is in 5 or 8 positions. The magnitude of splitting and

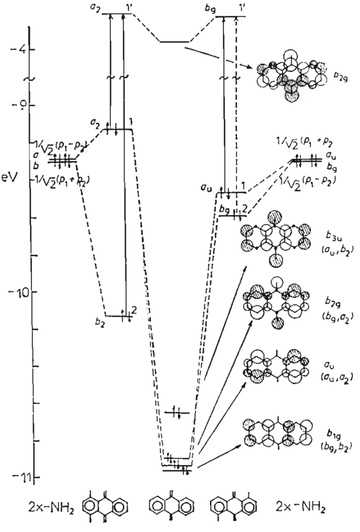


FIG. 6

The MO correlation graph of α,α'-diamino-9,10-anthraquinones for fragmentation into 9,10-anthraquinone and two α-NH_2 groups. (At the left side of the picture; instead of *a* and *b* should be a_2 and b_2)

the marked lowering of excitation energy of the first transition of 1,4-diamino-9,10-anthraquinone (as compared with the 1,5- and 1,8-isomers) can also be seen in the MO correlation graphs describing interaction between four highest occupied MOs of 9,10-anthraquinone and two $2p_\pi$ MOs of amino groups expressed as their linear combinations (Fig. 6). With the 1,4-isomer, the symmetrical combination of $2p_\pi$ MOs of nitrogen atoms of amino groups does not interact with any of the MOs of 9,10-anthraquinone, whereas the antisymmetrical combination interacts with two MOs, which results in large splitting of the first two occupied MOs and a marked lowering of excitation energy of the first electronic $\pi\pi^*$ transition. With the 1,5-isomer, each of the linear combinations of $2p_\pi$ MOs of nitrogen atoms of α-amino groups only interacts with one occupied MO of 9,10-anthraquinone, which results in an only small splitting of the highest occupied MOs of this isomer and in higher excitation energy of the first $\pi\pi^*$ electronic transition (as compared with the 1,4-isomer).

Graphical representation of the first two $\pi\pi^*$ transitions of α,α′-diamino-9,10-anthraquinones in the MO correlation graphs is fully justified with respect to high weight coefficient of the $\pi\pi^*$ excited configurations $1 \rightarrow 1'$ and $2 \rightarrow 1'$ in the first and the second singlet $\pi\pi^*$ transitions of α,α′-diamino derivatives of 9,10-anthraquinone.

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