ELECTRONIC ABSORPTION, FLUORESCENCE AND POLARISATION SPECTRA OF 1- AND 2-AMINO-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.

Absorption frequency-dependent polarisation spectra of fluorescence (APF) and dichroism on oriented polyvinyl alcohol sheets have been measured and used as a basis for interpretation of absorption spectra of 1- and 2-amino-9,10-anthraquinones in the region 250—600 nm. Character of the excited states was determined by the method of configuration analysis (PPP–CA).

Disperse quinoid dyestuffs represent a significant group among commercial dyestuffs. This class involves mono- and diamino-9,10-anthraquinones and their derivatives. Important properties for application of these dyestuffs are their hue, light fastness and character of their interaction with substrate and its influence on coloristic properties of the dyestuff. These properties are determined first of all by energy and character of the excited electronic states which depend on electronic structure of the molecule. Therefore, for understanding and explanation of relations between electronic structure and the properties connected with the excited electronic states of the molecule it is necessary to investigate first of all the relation between electronic structure of the dyestuff and characteristics of its electronic states or transitions.

Shcheglova and coworkers[1] studied experimentally the absorption and luminescence spectra of mono- and diamino-9,10-anthraquinones. They used the shift of absorption bands for discussion of H-bond effect on energy of electronic states. Also they discuss the relation between structure of the mentioned compounds and their luminescence properties. Popov and coworkers[2] discussed energies of the excited states of 1-amino- and 1-hydroxy-9,10-anthraquinones, the substituent effect being

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considered as a perturbation. Shcheglova and coworkers[3] studied the H-bond effect on fluorescence of 1-amino-2-alkyl-9,10-anthraquinone and the alkyl steric effect on the electronic spectrum. A systematic study of solvent effect on electronic spectra of monosubstituted 9,10-anthraquinones was carried out by Yoshida and Takabayashi[4] and Issa and coworkers[5]. The authors discussed effects of H-bond, solvent polarity, and character of substituent on shift of the absorption bands, the longest-wave band being interpreted as the charge-transfer transition from substituent to anthraquinone. Dähne & Leupold[6], on the contrary, interpreted the first band of 9,10-anthraquinone derivatives as a consequence of interaction of polymethine fragments. Spruit[7] differentiates between the delocalized "fundamental bands" and localized "partial bands". Similarity of spectra of 9,10-anthraquinone and those of correspondingly substituted 1,4-naphthoquinones led the author[7] to a conclusion that two 1,4-naphthoquinoid halves of a substituted 9,10-anthraquinone absorb independently, *i.e.* spectrum of 9,10-anthraquinone is considered to be a superposition of two spectra of 1,4-naphthoquinone. In accordance therewith intensity of the first absorption band in spectra of 1,5- and 1,8-disubstituted 9,10-anthraquinones is approximately two times greater than that of 1-substituted anthraquinone (additivity rule)[7-9]. Absorption and fluorescence spectra of amino-9,10-anthraquinones related to photochemical properties of the latter were also studied by Allen and coworkers[10], McKellar[11] and Davies and coworkers[12]. Labhart[13] studied polarisation spectra of some disubstituted anthraquinones by the method of electrically induced dichroism. Zaicev and Allenov[14] studied 9,10-anthraquinone derivatives by PPP method. Inoue and coworkers[15] used also the PPP method for interpretation of spectra of amino- and hydroxy-9,10-anthraquinones and measured dichroism on polyvinylalcohol sheets. Kogo and coworkers[16] investigated the relation between constitution and colour in a series of mono- and polysubstituted 9,10-anthraquinone derivatives using the PPP method with variable β^c and γ integrals (approximation of quasireal geometry). Position of the first absorption band of the spectrum was correlated with electron-donor ability of the substituent (expressed by ionisation potential of the donor). Character of transitions was determined on the basis of changes of expansion coefficients in the HOMO and LUMO and from changes of π-electron density in the ground and excited electronic configurations at the electron-donor and electron-acceptor centres of the molecule. The H-bond effect was modelled by the change of ionisation potential and electron affinity at the respective centres. Morley[17] used the CNDO/2 method for calculation of electronic structure of 1- and 2-amino-9,10-anthraquinone.

In Part VIII of this series[18] we investigated character of electronic states, applying the so called configuration analysis (PPP–CA) to anthraquinone and some of its derivatives (2-NO_2, 1-NH_2, 2-NH_2) and to indanthrone and isoindanthrone; furthermore we used[19] the same method in a study of character of states of a series of polynuclear *p*-quinones. The method of configuration analysis proved useful for explanation of relations between structure and spectrum. In the communication[18] attention was focused to the 9,10-anthraquinone chromofore, whereas spectra of 9,10-anthraquinone derivatives were only interpreted from the point of view of applicability of the configuration analysis to these systems, a deeper analysis of the experimental spectrum and the corresponding parameter study within the framework of PPP method being not carried out.

The present communication attempts to do a detailed interpretation of electronic spectra of 1- and 2-amino-9,10-anthraquinones on the basis of results of measurements of dichroism on polyvinylalcohol sheets and those of polarisation of fluorescence by photoselection method and on the basis of parameter study and configuration analysis. The subsequent communications will bring interpretation of electronic spectra of all diamino-9,10-anthraquinones on the basis of the above-mentioned experimental and theoretical methods.

EXPERIMENTAL

The compounds studied were synthetized in Research Institute of Organic Syntheses, Pardubice-Rybitví. Their purity was checked by chromatography and by excitation fluorescence spectra.

The fluorescence spectra and the APF spectra were measured at 77 K with a recording spectrophotometer Hitachi Perkin–Elmer MPF-2A equipped with a device for collecting data on a punched tape. The results of measurement were processed with a computer. The fluorescence spectra are corrected.

For measurement of the dichroic spectra we used polyvinyl alcohol of fa Waker. The measured substance was dissolved in the PVA sheet by submersing the sheet in solution of the substance in 95% aqueous ethanol. After sufficient swelling, the sheet was immediately stretched to sextuple of its original longitude. As PVA absorbs considerably especially in UV region, correction to the base line is necessary in the absorption spectra measurements. The reference sheet was swelled in pure solvent and treated similarly as the sample sheet. The measurement was carried out with a Perkin–Elmer 356 spectrophotometer with attached device for data collecting and processing. A dichroic polarisation filter was used as the polarisator enabling to measure up to the wave length of 250 nm. The correction to the base line, calculation of dichroism degree, and drawing of all the curves were carried out by a computer with recorder.

The absorption spectra were measured at 88 K in a mixture ethanol–methanol 4 : 1 and at room temperature in benzene. The measurement was carried out with the PE 356 spectrophotometer, too.

Calculations

The theoretical spectral characteristics were obtained by the Pariser–Parr–Pople (PPP) method. The calculations were carried out in approximation of quasi-real geometry with variable β^c and γ integrals, the starting geometry being considered ideal, *i.e.* all bond lengths and angles equal to 0·14 nm and 120°, respectively. The bicentric core integrals $\beta^c_{\mu\nu}$ were calculated from the formula

$$\beta^c_{\mu\nu} = b \, . \, \beta^c_{\mu\nu} \exp\left(-1{\cdot}862 r_{\mu\nu} + 2{\cdot}597\right);$$

the parameter b is considered adjustable and was determined on the basis of the parameter study in the case of C=O and C—NH_2 bonds. The $r_{\mu\nu}$ bond length between two adjacent atoms was calculated in each iteration by the Julg formula[20]

$$r_{\mu\nu} = (1{\cdot}517 - 0{\cdot}18p_{\mu\nu})\,(6{\cdot}5/(\vartheta_\mu + \vartheta_\nu))^{1/2}\,,$$

where $p_{\mu\nu}$ means the π-electronic bond order, and ϑ_μ and ϑ_ν are the Slater exponents of $2p_z$ atomic orbitals at the atoms μ and ν, respectively. The monocentric repulsion integrals $\gamma_{\mu\mu}$ were obtained by the Pariser approximation[21]

$$\gamma_{\mu\mu} = I_\mu - A_\mu\,,$$

where I_μ and A_μ mean the ionisation potential and the electron affinity, respectively, of the atom μ in the given valence state and environment. The bicentric repulsion integrals $\gamma_{\mu\nu}$ $(\mu \neq \nu)$ were calculated by the Mataga & Nishimoto approximation[22]. The parameters used are given in Table I.

The configuration interaction involves the singlet monoexcited configurations corresponding to transitions between five highest occupied and five lowest unoccupied MOs.

Character of electronic states and transitions is discussed in terms of local (LE) states and transitions, respectively, at the 9,10-anthraquinone skeleton and in terms of charge-transfer (CT) states and transitions, respectively, connected with charge transfer from amino group to anthraquinone skeleton. Character of the $\pi\pi^*$ singlet electronic transitions was determined from changes of LCI π-electronic densities at the respective subsystems (9,10-anthraquinone, amino group) in the given $S_0 \rightarrow S_n$ transition[23]. Character of the $\pi\pi^*$ electronic excited states was determined with the use of the configuration analysis described elsewhere[24,25] and discussed in the VIIIth communication of this Series[18] for quinoid systems.

The numbers given in the MO diagrams are squares of matrix elements of **B** matrix representing an LCMO (linear combination of molecular orbitals) description of the delocalized π-MO (total π system) in terms of pars orbitals (atomic or molecular orbitals of the fragments)[24].

TABLE I

The parameters used in calculation of aminoanthraquinones by PPP method

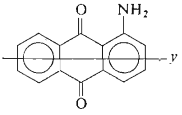
Atomic core	Z_π	I_μ, eV	A_μ, eV	ϑ_μ	b
C^+	1	11·42	0·58	3·25	1·0 (C—C)
O^+	1	17·70	2·47	3·95	0·8 (C=O)[a] 0·7 (C=O)[b]
N^{+2}	2	27·30	9·30	2·67	0·7 (C—N)[c]

[a,b,c] The values were obtained from the parameter study and are adjusted to optimum agreement with position of the first band in the absorption spectrum; [a] the value applies to the both carbonyl groups, if NH_2 group is at α position and for the non-substituted 9,10-anthraquinone; [b] the value applies to the both carbonyl groups, if NH_2 group is at β position; [c] the value applies to both α- and β-NH_2 substituent; $\beta^0_{\mu\nu} = -2{\cdot}318$ eV.

RESULTS AND DISCUSSION

Analysis of absorption spectrum with the help of measurement of APF spectrum and determination of dichroism degree on oriented sheets make it possible to assign theoretical transitions to absorption bands. This assignment is easier, if the molecule investigated has C_{2v} or D_{2h} symmetry when the moments of electronic transitions are mutually perpendicular or parallel. In molecules of other symmetries the moments of electronic transitions can have any direction in the plane of the molecule, and the assignment is more difficult and not always unambiguous due to overlap of bands and depolarisation effects.

Experimental spectral curves along with theoretical PPP results are given in Fig. 1 for 1-amino-9,10-anthraquinone (scheme *A*). The theoretical transitions are polarized



A

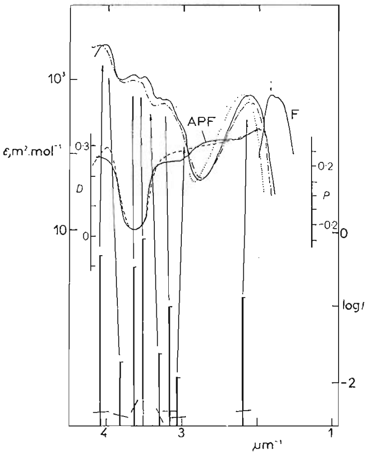


FIG. 1

Electronic spectrum of 1-amino-9,10-anthraquinone; (———) the absorption spectrum in ethanol-methanol mixture 4 : 1 at 88 K; (*F*—) the fluorescence spectrum in ethanol-methanol mixture 4 : 1 at 77 K (the small arrow denotes the fluorescence 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 on the oriented polyvinyl alcohol sheet; (······) the absorption spectrum in benzene; (-----) the dichroic curve on the oriented polyvinyl alcohol sheet; *D* the dichroism degree; *P* degree of polarisation of fluorescence; the vertical lines denote the theoretical transitions calculated by the PPP method, the short lines represent directions of transition moments with respect to *y*-axis; the assignment of the individual transitions to the respective absorption bands is denoted by arrows either almost parallel to y-axis or almost perpendicular to it, although the molecule has C_s symmetry only. This fact along with clean-cut character of the absorption spectrum and polarisation curves enable a fairly unambiguous assignment of eight $\pi\pi^*$ electronic transitions. In the region 1·8 to 2·7 μm^{-1} there is a broad absorption band, and both the APF and D curves have nearly constant value in this region, hence this band is assigned to the first $\pi\pi^*$ transition polarized approximately along y-axis. In the region 2·8 to 3·4 μm^{-1} there are two overlapped bands whose polarisations are mutually almost parallel and nearly parallel to that of the first band (the second of the two bands forms a shoulder in the absorption curve obtained with alcoholic mixture at low temperature); these bands are assigned to the second and the third $\pi\pi^*$ transitions. In the region 3·4 to 3·7 μm^{-1} both the APF and D curves show a marked minimum, which indicates the presence of one or several bands with mutually parallel (but perpendicular to the first band) polarisation. Three transitions are predicted here by theory in accordance with experiment as to the direction of polarisation. In the region 3·7 to 4·2 μm^{-1} of the absorption curve the polarisation approximately agrees with direction of the first band (the seventh and eighth $\pi\pi^*$ transitions according to the PPP results).

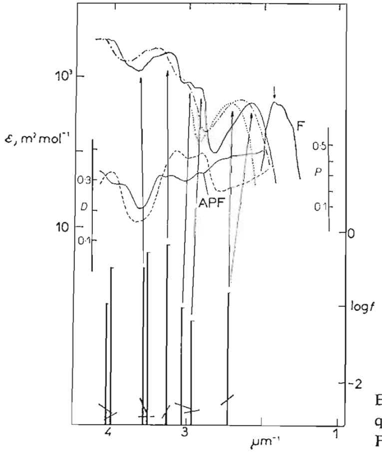
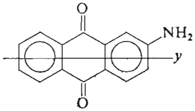


FIG. 2

Electronic spectrum of 2-amino-9,10-anthraquinone (for explanation of symbols see Fig. 1)

Fig. 2 represents experimental spectra and theoretical PPP results for 2-amino-9,10-anthraquinone (scheme *B*). In the region 2·0 to 2·7 μm^{-1} there is a broad absorption band and both the APF and D curves have practically constant value here. To this band we assign the first $\pi\pi^*$ transition whose theoretical energy value agrees well with the experimental spectrum measured in benzene. The moment of the first $\pi\pi^*$ transition is directed approximately along conjugation between amino groups and 10-carbonyl group. In the region 2·7 to 3·1 μm^{-1} it is possible, on the basis of the polarisation curves, to identify two absorption bands with mutually almost parallel polarisation. These bands are connected with the second and the third $\pi\pi^*$ transitions which appear as a shoulder at 3·0 μm^{-1} in the spectrum measured in polyvinyl alcohol sheet, whereas in alcoholic mixture at low temperature the two bands are separated. A marked minimum in the polarisation curves at 3·6 μm^{-1} indicates absorption bands polarized almost perpendicularly to the second band; they could be connected with the fourth and the fifth transitions. Assignment of the other bands is problematic because of large overlap of the bands in the absorption spectrum, and, mainly, because there are different directions of transition moments of 2-amino-9,10-anthraquinone in contrast to the 1-amino isomer.



B

It is noteworthy that the APF and the D curves have practically identical course in the case of the 1-amino isomer, whereas in the case of the 2-amino isomer they are different in course. This difference is caused by the fact that the measurement of excitation polarisation spectrum of fluorescence involves determination of direction of moments of $S_0 \rightarrow S_n$ transitions with respect to the $S_0 \rightarrow S_1$ transition, *i.e.* transition to the state from which fluorescence takes place. However, measurement of dichroism on an oriented sheet involves determination of direction of transition moments with respect to effective axis of orientation of the molecule. If the $S_0 \rightarrow S_1$ transition moment is oriented along the effective axis of orientation, then the APF and the D curves have practically identical course; if the $S_0 \rightarrow S_1$ transition moment is oriented perpendicularly to the effective axis of orientation, then the APF curve shows mirror symmetry with respect to the D curve. General orientation of direction of the $S_0 \rightarrow S_1$ transition moment with respect to effective axis of orientation results in different course of the two polarisation curves. It can be presumed that the effective orientation axis of 1- and 2-amino-9,10-anthraquinones is practically identical with

y-axis. In the case of 1-amino isomer the deviation of the $S_0 \rightarrow S_1$ transition moment from y-axis is 12° (Table II), and the APF and the D curves show identical course according to expectation. However, in the case of 2-amino derivative the mentioned

TABLE II

The 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. The y-axis is perpendicular to connecting line of C=O bonds

n	Symmetry	$\Delta^1 E_n(S_0 \rightarrow S_n)$		$\log f$	$\sphericalangle(\mathbf{M}, y)$	The first two main configurations
		eV	μm^{-1}			
			9,10-Anthraquinone			
1	B_{3g}	3·798	3·064	f	—	4,1′ (98·9)
2	B_{2u}	3·988	3·217	−0·265	∥	3,1′ (99·9)
3	A_g	3·993	3·221	f	—	2,1′ (90·1)
4	B_{1u}	4·348	3·508	−0·037	⊥	1,1′ (97·8)
5	B_{2u}	4·969	4·009	−0·277	∥	4,2′ (67·2); 1,4′ (18·5)
6	A_g	5·163	4·165	f	—	1,2′ (84·0)
7	B_{1u}	5·571	4·495	−1·675	⊥	2,2′ (94·2)
8	B_{3g}	5·660	4·566	f	—	3,2′ (100)
			1-Amino-9,10-anthraquionone			
1	—	2·688	2·169	−0·854	192°	1,1′ (93·2)
2	—	3·773	3·044	−1·918	2°	4,1′ (88·2)
3	—	3·902	3·148	−0·970	178°	3,1′ (81·3)
4	—	4·109	3·315	−1·597	97°	1,2′ (47·3); 2,1′ (20·5)
5	—	4·347	3·507	−0·240	95°	2,1′ (57·2); 5,1′ (23·8)
6	—	4·467	3·604	−0·538	250°	5,1′ (48·3); 1,2′ (19·7)
7	—	4·729	3·815	−1·651	320°	1,3′ (63·7); 5,1′ (8·1)
8	—	5·049	4·073	−0·414	355°	2,2′ (29·6); 4,2′ (29·5)
			2-Amino-9,10-anthraquinone			
1	—	3·015	2·433	−0·821	221°	1,1′ (86·9)
2	—	3·635	2·933	−1·160	188°	4,1′ (72·9); 1,2′ (9·7)
3	—	3·777	3·047	−0·926	169°	3,1′ (71·7); 4,1′ (11·2)
4	—	4·017	3·241	−0·304	86°	2,1′ (63·8); 5,1′ (16·3)
5	—	4·330	3·493	−0·357	356°	1,2′ (55·3); 1,4′ (11·7)
6	—	4·424	3·569	−0·625	112°	5,1′ (61·3); 2,1′ (24·6)
7	—	4·944	3·989	−0·566	17°	2,2′ (61·9); 1,3′ (10·4)
8	—	5·018	4·048	−0·941	317°	1,3′ (40·0); 4,2′ (18·4)

deviation is 41° and the APF and D curves show different course. From this point of view it can be understood that the D curve shows the maximum dichroism degree in the region of the second and the third transition, whereas the APF curve shows always the maximum value of polarisation degree in the region of the first transition. The both aminoanthraquinones show a little intesive fluorescence; the fluorescence spectra have approximate mirror symmetry to the first absorption bands.

The *b* parameter in the formula for calculation of the bicentric core integrals $\beta_{\mu\nu}^{\text{core}}$ of the C=O and C—NH$_2$ bonds was determined on the basis of a parameter

TABLE III

Character of transitions of amino-9,10-anthraquinones determined from changes of the LCI π-electron charges in the subsystems during $S_0 \rightarrow S_n$ transition; amino group and anthraquinone are considered as the subsystems

Transition	Character	% Transition type		Δq_S[a]	Δq_{CT}[b]	Δq_{LE}[c]
		1-Amino-9,10-anthraquinone				
$S_0 \rightarrow S_1$	CT	83	α-NH$_2$→9,10-AQ		0·63	—
	LE	17	9,10-AQ	0·76	—	0·13
$S_0 \rightarrow S_2$	CT	3	α-NH$_2$→9,10-AQ		0·02	—
	LE	97	9,10-AQ	0·65	—	0·63
$S_0 \rightarrow S_3$	CE	1	α-NH$_2$→9,10-AQ		0·004	—
	LE	99	9,10-AQ	0·50	—	0·50
$S_0 \rightarrow S_4$	CT	68	α-NH$_2$→9,10-AQ		0·41	—
	LE	32	9,10-AQ	0·60	—	0·19
		2-Amino-9,10-anthraquinone				
$S_0 \rightarrow S_1$	CT	69	β-NH$_2$→9,10-AQ		0·46	—
	LE	31	9,10-AQ	0·66	—	0·21
$S_0 \rightarrow S_2$	CT	10	β-NH$_2$→9,10-AQ		0·06	—
	LE	90	9,10-AQ	0·56	—	0·50
$S_0 \rightarrow S_3$	CT	3	β-NH$_2$→9,10-AQ		0·02	—
	LE	97	9,10-AQ	0·51	—	0·49
$S_0 \rightarrow S_4$	CT	21	β-NH$_2$→9,10-AQ		0·10	—
	LE	79	9,10-AQ	0·49	—	0·38

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

study, the criterion consisting in agreement between excitation energy of the first transition and the first absorption band. The resulting values of parameters are given in Table I. In the case of 1-amino-9,10-anthraquinone the strong internal H-bond was not considered separately, and, therefore, the parameter *b* represents a sum of the internal H-bond effect and effect of position of NH_2 substituent. Thus it is quite logical to use different parameters for NH_2 substitution at 1 and 2 positions. Table II gives theoretical spectral characteristics of 1- and 2-amino-9,10-anthraquinones for the first eight $\pi\pi^*$ electronic transitions. From Figs 1 and 2 it follows that the theory (PPP) agrees well with experiment.

The theoretical spectral characteristics (energy, probability and direction of moment of electronic transitions), however, give no information about character of the

TABLE IV

The results of configuration analysis (PPP–CA) with 9,10-anthraquinone as reference system (the excited states S_n^0), NB means non-bonding configuration of the ground state of the system (9,10-anthraquinone + NH_2 group); r_M is the index expressing the 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	% CT	% r_M
			1-Amino-9,10-anthraquinone							
—	—	S_0	88	0	0	0	0	0	10	98
2·169	−0·854	S_1	2	1	16	10	0	0	59	90
3·044	−1·918	S_2	0	81	4	0	1	0	3	89
3·148	−0·970	S_3	0	1	42	44	0	0	1	88
3·315	−1·597	S_4	3	5	1	5	27	1	36	89
3·507	−0·240	S_5	1	1	7	9	52	1	13	88
3·604	−0·538	S_6	1	0	17	19	8	0	35	90
3·815	−1·651	S_7	0	0	1	1	0	12	41	91
4·073	−0·414	S_8	0	0	0	0	0	49	1	88
			2-Amino-9,10-anthraquinone							
		S_0	90	0	0	0	0	0	8	98
2·433	−0·821	S_1	1	31	9	4	4	0	41	92
2·933	−1·160	S_2	0	37	37	9	0	0	8	92
3·047	−0·926	S_3	0	1	30	56	0	0	2	91
3·241	−0·304	S_4	0	13	5	7	55	1	10	91
3·493	−0·357	S_5	2	1	1	3	7	20	37	91
3·569	−0·625	S_6	1	6	8	9	21	1	35	91
3·989	−0·566	S_7	0	0	0	1	0	7	14	91
4·048	−0·941	S_8	1	0	0	0	1	35	23	91

$\pi\pi^*$ electronic transitions which could serve as a basis for discussion of deeper relationships between structure and electronic spectrum of the molecule investigated. We determined the character of the transitions in two ways: by analysis of changes of the LCI π-electron densities in the fragments at the given excitation[23] and by the configuration analysis. Nitrogen atom of NH_2 group was considered to be the electron-donor centre, the whole anthraquinone skeleton being the electron-acceptor centre. Thus we have CT transitions with charge transfer from amino group to anthraquinone and local transtions (LE) in the anthraquinone subsystem. Table III gives characters of the $\pi\pi^*$ transitions obtained from changes of the LCI π-electron densities at the various above-mentioned molecular subsystems during the $S_0 \rightarrow S_n$ transi-

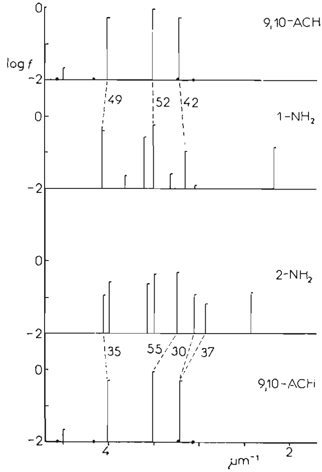


FIG. 3

The correlation graph of singlet excited states of 1- and 2-amino-9,10-anthraquinones (with 9,10-anthraquinone as the reference system) constructed on the basis of the PPP–CA results; full circle denotes the forbidden transitions of 9,10-anthraquinone

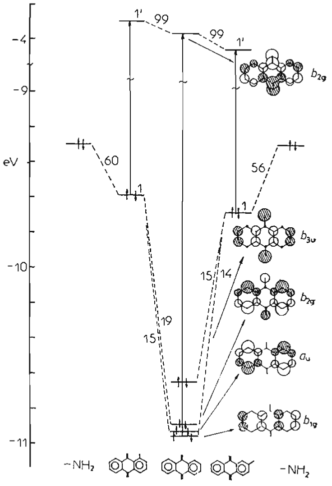


FIG. 4

The correlation graph of MOs of mono-amino-9,10-anthraquinones for the fragmentation into 9,10-anthraquinone and amino group tion ($n = 1-4$). The proportion of the π-electron charge transferred in the given transition from amino group to 9,10-anthraquinone skeleton (Δq_{CT}) and redistributed in the 9,10-anthraquinone subsystem (Δq_{LE}) referred to overall charge migration (Δq_S) is expressed in per cent. The data of Table III show that the first transition of the two derivatives is connected with significant charge transfer, the transition in the 1-amino isomer having a more marked CT character than that in the 2-amino isomer. The next two transitions of the both isomers have a pronounced character of local transitions in 9,10-anthraquinone, and they are thus "anthraquinone transitions". The fourth transition in the 1-amino isomer has a CT character again, even though somewhat weaker as compared with the first transition. The fourth transition in the 2-isomer has a predominantly local character with a somewhat higher proportion of CT transition as compared with the second and the third transitions.

Table IV gives the results of configuration analysis (PPP–CA). In the case of 1-amino derivative the S_1 state has a predominant CT character, in the case of the 2-isomer there are two contributions to the first singlet excited state: besides CT configuration also a considerable contribution of "local" $S_1^0(^1B_{3g})$ state; transition to the latter is forbidden in the case of nonsubstituted 9,10-anthraquinone. The second transition in the 1-amino derivative is an almost pure transition to the LE state $S_1^0(^1B_{3g})$, that in the 2-isomer represents a "mixture" of transitions to the LE states $S_1^0(^1B_{3g})$ and $S_2^0(^1B_{2u})$. As the transition to $^1B_{3g}$ state is forbidden, the main contribution to intensity of the second band in spectrum of the 2-amino derivative is made by local transition to the $^1B_{2u}$ state of the reference system; this transition is polarized in direction of y-axis, and thus it can be expected that the second transition in 2-amino-9,10-anthraquinone will be polarized along y-axis, too, which agrees with the dichroic curve D in Fig. 2. Also in accordance with the curve D is the fact that predominant contribution to intensity of the fourth band of 2-amino-9,10-anthraquinone is made by the allowed transition to the LE state $^1B_{1u}$ which is polarized along z-axis, *i.e.* perpendicularly to the second and the third transitions. The results of configuration analysis also agree with polarization of the fifth and the eighth transitions of 1-amino-9,10-an-

TABLE V

The SCF–MO excitation energies of 1- and 2-amino-9,10-anthraquinones

Isomer	$V_{11'}$, eV	$\Delta\varepsilon$, eV (LUMO–HOMO)	$J_{11'} - 2K_{11'}$, eV
1	2·826	5·694	−2·868
2	3·199	5·629	−2·430

thraquinone (the former transition is predominantly to LE state $S_4^0(z)$, the latter to LE state $S_5^0(y)$). Fig. 3 represents correlations between the transitions in 1- and 2-amino-9,10-anthraquinones and 9,10-anthraquinone.

The values r_M (in %) of Table IV show that the fragmentation of amino-9,10-anthraquinones into amino group and 9,10-anthraquinone represents the 2-isomer better than the 1-isomer. Obviously this fact is due to the well-known fact that 2-amino group is less conjugated with the 9,10-anthraquinone skeleton than is 1-amino group. Perceptible share of CT configuration in the ground states of the two isomers is noteworthy.

Useful information about the first intensive absorption band of the spectrum (whose position is decisive for colour of the compound) can also be obtained from the MO correlation graph (Fig. 4). The first band in spectra of 1- and 2-amino-9,10-anthraquinones corresponds to electron transition from the HOMO to the LUMO. Whereas the LUMO of the two amino derivatives corresponds practically fully to the LUMO of the parent system, *i.e.* 9,10-anthraquinone (see the numbers in the MO diagram), the main contribution to the HOMO of the both isomers is made by $2p_\pi$ MO of nitrogen of NH_2 group, but contributions of other MOs cannot be neglected *viz.* that of the second (b_{2g}) and the third (a_u) occupied MOs of 9,10-anthraquinone in the case of the 1-isomer, and that of the first (b_{3u}) and the fourth (b_{1g}) occupied MOs of 9,10-anthraquinone in the case of the 2-isomer. Only the given MOs of 9,10-anthraquinone exhibit an efficient overlap with $2p_\pi$ MO of nitrogen of NH_2 group. The MO diagrams also show a marked CT character of the first $\pi\pi^*$ transition (an almost "pure" 1,1′ transition) for the both amino derivatives.

The one-electron model and energy difference between the HOMO and the LUMO, however, do not allow to make conclusion about excitation energy of the first $\pi\pi^*$ transition. From Fig. 3 it is seen that even the order of colour hues of the two isomers given by the simple MO model contradicts the experiment. Of course, a correct order can already be obtained by introduction of electron repulsion in the calculation (Table V), if

$$V_{11'} = \Delta\varepsilon(\mathrm{LUMO} - \mathrm{HOMO}) + (J_{11'} - 2K_{11'})\,.$$

The difference in magnitude of the repulsion terms of the two isomers originates probably from different CT character of the $1 \rightarrow 1'$ transition. In analogy to azulenes[26], the transition with stronger CT character (1-amino-9,10-anthraquinone, Tables II–IV) is connected with lower excitation energy, although the order of $\Delta\varepsilon$ values is opposite.

With respect to the marked CT character of the first transition it can be expected that solvent polarity and possibility of H-bond formation will affect considerably position of the first band in the spectrum. The internal H-bond in 1-amino-9,10-

-anthraquinone is very stable, hence it can be expected that "saturation" by internal H-bond in the 1-amino derivative will reduce its interactions with solvent molecules as compared with the 2-isomer. This result agrees with experiment (*cf.* the shift of the first band in benzene and alcohol for the 1- and 2-isomers, Figs 1 and 2).

REFERENCES

1. Shcheglova N. A., Shigorin D. N., Dokunichin H. S.: Zh. Fiz. Khim. *42*, 2724 (1968).
2. Popov K. R., Platonova N. V., Smirnov L. V.: Opt. Spektrosk. *32*, 1097 (1972).
3. Shcheglova N. A., Nezhelskaya R. A., Shigorin D. N., Galitsina L. V.: Zh. Fiz. Khim. *48*, 276 (1974).
4. Yoshida Z., Takabayashi F.: Tetrahedron *24*, 913 (1968).
5. Issa I. M., Issa R. M., Idriss K. A., Hamman A. M.: Indian J. Chem. *14B*, 117 (1976).
6. Dähne S., Leupold D.: Angew. Chem. *78*, 1029 (1966).
7. Spruit C. J. P.: Rec. Trav. Chim. *68*, 325 (1949).
8. Peters R. H., Summer H. H.: J. Chem. Soc. *1953*, 2101.
9. Egerton G. S., Roach A. G.: J. Soc. Dyers Colour. *74*, 401 (1958).
10. Allen N. S., Bentley P., McKellar J. F.: J. Photochem. *5*, 225 (1976).
11. McKellar J. F.: Radiat. Res. Rev. *3*, 141 (1971).
12. Davies A. K., McKellar J. F., Phillips G. O.: Proc. Roy. Soc. (London) *A323*, 69 (1971).
13. Labhart H.: Chimia *15*, 20 (1961).
14. Zajcev B. H., Allenov V. M.: Zh. Prikl. Spektrosk. *20*, 109 (1974).
15. Inoue H., Hoshi T., Yoshino J., Tanizaki Y.: Bull. Chem. Soc. Jap. *45*, 1018 (1972); *46*, 380 (1973).
16. Kogo Y., Kikuchi H., Matsuoka M., Kitao T.: J. Soc. Dyers Colour. *96*, 475 (1980).
17. Morley J. C.: J. Chem. Soc., Perkin Trans. 2, *1972*, 1223.
18. Fabian J., Nepraš M.: This Journal *45*, 2605 (1980).
19. Nepraš M., Fabian J., Titz M.: This Journal *46*, 20 (1981).
20. Julg A.: J. Chim. Phys. Physicochim. Biol. *55*, 413 (1958); *57*, 19 (1960).
21. Pariser R.: J. Chem. Phys. *21*, 568 (1953).
22. Nishimoto K., Mataga N.: Z. Phys. Chem. (Wiesbaden) *12*, 335 (1957); *13*, 140 (1957).
23. Nepraš M., Titz M.: Int. J. Quantum Chem. *16*, 543 (1979).
24. Baba H., Suzuki S., Takemura T.: J. Chem. Phys. *50*, 2078 (1969).
25. Fabian J.: Signalaufzeichnungsmaterialien *6*, 307 (1978).
26. Michl J., Thulstrup E. W.: Tetrahedron *32*, 205 (1976).

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