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An INDO/S Study of the Second $\pi\pi^*$ Transition in the Spectra of 1,4-Diaminoanthraquinones Responsible for their Green Hue

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ABSTRACT

The INDO/S approach is used to study the structure/spectra relationship for some N,N'-disubstituted 1,4-diaminoanthraquinones. The calculated intensity and position of the short-wavelength absorption band depend on the molecular conformation, in agreement with the experimental data. The reflection spectra of crystalline 1,4-bisanilinoanthraquinone and 1,4-bis(mesitylamino)anthraquinone are reported and the crystal structure of the latter compound has been determined. © 1998 Elsevier Science Ltd

Keywords: diaminoanthraquinone, crystal structure, INDO/S, reflection spectra.

1 INTRODUCTION

It is well known that the visible spectra of 1,4-bis(arylamino)anthraquinones have an additional maximum at 390–420 nm responsible for the green colour of these compounds [1]. The displacement of the aryl groups from the plane of the anthraquinone system (e.g. due to their *ortho*-substitution) produces the hypsochromic shift of this maximum accompanied by the loss of

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absorptivity [2, 3]. Replacement of one aryl group by an alkyl or H atom has the same effect [3, 4]. On the contrary, extension of aryl π-systems, especially with π-acceptors, shifts this maximum bathochromically and this band increases in intensity [5–7].

Whilst the nature of the lowest $\pi\pi^*$ excited state of 1,4-diaminoanthraquinones, associated with the long-wavelength 'red' absorption maximum above 600 nm, has been the subject of several experimental [8–10] and theoretical [11, 12] investigations, no systematic studies of the nature and behavior of the additional 'blue' maximum have been reported in the literature.

The purpose of this work is to study, on the semiempirical (INDO/S) level, correlations between the composition and conformation of N,N′-disubstituted 1,4-diaminoanthraquinones on the one hand, and the position and intensity of the 'blue' maximum on the other. Since the semiempirical methods of the MNDO family were found to be incapable of modeling the conformations of arylamino groups in anthraquinone derivatives [13], molecular models were built up on the basis of X-ray structural data for related compounds. We have recently presented the results of structural studies of 1,4-bisanilinoanthraquinone [14] (**I**) and 1-hydroxy-4-(*p*-toluidino)anthraquinone [13]. Because the structures of *o*-substituted α-arylaminoanthraquinones are still unknown, the crystal structure of 1,4-bis(mesitylamino)anthraquinone (**II**) has been determined. In addition, the visible spectra of crystalline **I** and **II** are also reported.

2 EXPERIMENTAL

I and **II** obtained using established procedures were purified chromatographically and recrystallized from benzene.

Visible reflection spectra were recorded on a Specord M-40 spectrophotometer, X-ray measurements were carried out on an Enraf-Nonius CAD-4 diffractometer (Mo Kα radiation, ω-scan technique). Compound **II** gave crystals belonging to the monoclinic space group $P2_1/n$, $a = 12.419(3)$, $b = 10.593(3)$, $c = 19.494(4)$ Å, $\beta = 96.03(2)°$, $V = 2550$ Å^3, $Z = 4$, $R(F)$ for 1817 reflections with $I > 2\sigma(I)$ and $R(F^2)$ for all 3982 reflections are 0.059 and 0.139, respectively. The structure was solved by direct methods using SHELXS-96 [15] and refined with SHELXL-93 [16]. All non-H atoms are given anisotropically and hydrogens were refined isotropically. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The molecular structure of II is presented in Fig. 1, and selected geometrical parameters are given in Table 1.

Calculations on the INDO level were carried out with the GRINDOL [17] and INDO-SDCI [18] programs. Standard parametrizations were used.

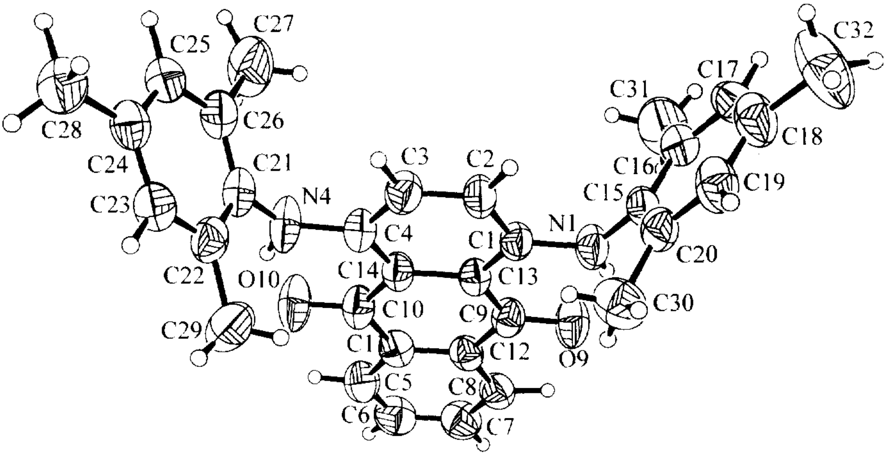


Fig. 1. ORTEX [30] plot of the 1,4-bis(mesitylamino)anthraquinone molecule.

TABLE 1

Selected Bond Lengths (Å), Bond Angles and Torsion Angles (°) for 1,4-bis(mesitylamino)anthraquinone (**II**) (see Fig. 1 for atom labels)

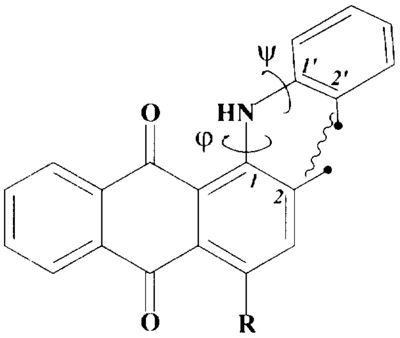
O9-C9	1.243(4)	C1-C13	1.403(4)	C9-C12	1.468(5)
O10-C10	1.241(4)	C1-C2	1.416(5)	C10-C14	1.446(5)
N1-C1	1.372(4)	C2-C3	1.343(5)	C10-C11	1.481(5)
N1-C15	1.416(4)	C3-C4	1.416(5)	C11-C12	1.392(5)
N4-C4	1.359(4)	C4-C14	1.411(5)	C13-C14	1.444(4)
N4-C21	1.432(5)	C9-C13	1.434(5)		
C1-N1-C15	124.9(4)	N4-C4-C3	119.7(4)	C12-C11-C10	120.5(4)
C4-N4-C21	124.2(4)	C14-C4-C3	117.5(3)	C11-C12-C9	120.5(4)
N1-C1-C13	121.7(4)	O9-C9-C13	122.9(4)	C1-C13-C9	120.7(3)
N1-C1-C2	119.0(4)	O9-C9-C12	117.6(4)	C1-C13-C14	118.9(3)
C13-C1-C2	119.3(3)	C13-C9-C12	119.6(3)	C9-C13-C14	120.5(4)
C3-C2-C1	121.2(4)	O10-C10-C14	122.9(4)	C4-C14-C13	120.6(4)
C2-C3-C4	122.6(4)	O10-C10-C11	118.1(4)	C4-C14-C10	119.6(3)
N4-C4-C14	122.8(4)	C14-C10-C11	119.0(3)	C13-C14-C10	119.8(4)
C15-N1-C1-C13	175.3(4)	N1-C1-C13-C9	−2.0(5)	C1-N1-C15-C20	80.8(5)
C15-N1-C1-C2	−6.3(6)	O9-C9-C13-C1	−2.4(6)	C1-N1-C15-C16	−103.1(4)
C21-N4-C4-C14	168.1(4)	N4-C4-C14-C10	−0.2(6)	C4-N4-C21-C26	93.3(5)
C21-N4-C4-C3	−11.6(6)	O10-C10-C14-C4	2.7(6)	C4-N4-C21-C22	−88.4(5)

Using GRINDOL we assumed the value of the adjustable parameter scaling β integrals to be 1. Bond lengths and angles in molecular models were optimized on the AM1 level with MOPAC 6.0 [19] by holding the torsion angles that define the conformation fixed; the anthraquinone moiety was constrained to be planar.

Details of structure determination, tables of atomic positional and thermal parameters, geometry and a listing of the results of semiempirical calculations are available from the authors upon request.

3 RESULTS AND DISCUSSION

X-ray structural studies of a number of α-arylaminoanthraquinones demonstrate that anthraquinone tricycles are essentially planar and that the N atoms lie not far from these planes, as well as not far from the planes of the aryl groups. Therefore, as the first approximation, the conformation adopted by the arylamino group is defined by two torsion angles, ϕ and ψ, which correspond to the rotations about the N1-C1 and N1-C1′ bonds, respectively, as depicted on the scheme. The values of ϕ and ψ for some α-arylaminoanthraquinones known from the literature are given in Table 2.



Scheme 1

TABLE 2

Torsion Angles ϕ(C2-C1-N1-C1′) and ψ(C1-N1-C1′-C2′) in Some Arylaminosubstituted Anthraquinones

Substituents	φ	ψ	*References*
1-amino, 4-anilino	11	39	20
1-hydroxy, 4-(*p*-toluidino)	11	44	13
1,5-bis[(4-ethylphenyl)amino]	5	51	21
1,4-bisanilino	2	51	14
	−1	60	
1,8-bisanilino	8	59	22
1,5-bisanilino	6	62	23
1-{[4-(dimethylamino)phenyl]amino},4-hydroxy	−1	71	24
1-{[4-(dimethylamino)phenyl]amino}	0	76	25
1,5-bis{[4-(pentyloxy)phenyl]amino}	−2	78	26
1,4-bis(mesitylamino)	−12	94	[a]
	−6	81	

[a] This work.

To achieve effective conjugation between the N1 lone pair and π-systems, both these angles ought to be as small as possible. Nevertheless, the reduction in ψ below 50° causes an increase in ϕ to produce a relief of the steric hindrance between the methylene groups at the 2 and 2′ positions. Calculations of the repulsion energy fulfilled in the '6-exp' approximation [27] demonstrate that the decrease of ϕ from 10° to 0° by holding the ψ angle fixed at 40° increases the repulsion energy by 33.5 kJ mol^{-1}. Thus the conformation with $\phi = 10°$ and $\psi = 40°$ was used in our further calculations as a standard one for sterically non-hindered molecules. Table 2 makes clear that the aryl groups with π-donating substituents form the greatest angles ψ, probably as a consequence of their reduced π-acceptor capacity.

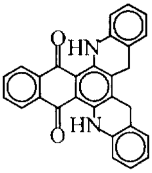
The INDO/S calculations performed for 1,4-diaminoanthraquinone and its N,N′ -derivatives predict two $\pi\pi^*$ electronic transitions assigned as 'red' and 'blue' absorption maxima. In full accordance with experimental data [10, 28], the long-wavelength transition is y axis polarized (long axis of tricycle), while the second one is oriented along the O9–O10 direction (z). In this region there are also several transitions of the $n\pi^*$ type, but their oscillator strengths are less than 0.001, so the above two mentioned $\pi\pi^*$ excited states will be referred to as the first and second singlet states. The results of calculations associated with the short-wavelength transition are summarized in Table 3 together with the related experimental data available from the literature.

Because of the large size of configuration space necessary to reproduce adequately the second singlet state (10 occupied and eight unoccupied orbitals), optimization of molecular geometry in this state was impossible and, thus we have restricted our considerations to the bond orders and atomic electron populations. The changes induced by excitation are presented in Fig. 2. Like the first singlet state, the second one is also a charge transfer state, but the charge, transferred from the N atoms, is not delocalized over the whole anthraquinone moiety, but is localized in the terminal ring. Charge transfer to the phenyl rings, especially to the *ipso* C atoms, takes place to a lesser degree. As a consequence, the calculated dipole moment of the second singlet state is smaller than that of the first singlet state: for **I**, 2.20 and 6.56 D, respectively. 1,4-Diaminoanthraquinone and its N,N′-diphenylderivative show no principal discrepancy in charge distribution in their first singlet states.

It is noteworthy that all computational approaches (our calculations on the INDO level as well as *ab initio* [12] and PPP [13] calculations) predict the appearance of the second transition even in the spectra of 1,4-diaminoanthraquinone and its N-alkylated derivatives, whilst among the non-arylated 1,4-diaminoanthraquinones this maximum was experimentally observed only for 1,4-bis[(1-phenylethyl)-amino]anthraquinone [29]. The calculations carried out for this molecule predict considerable changes in oscillator strengths

TABLE 3

Absorption Frequencies (ν) and Relative Intensities *(I)* of the Short-wavelength Band in Visible Spectra of Some Anthraquinone Derivatives

Compound	*INDO-calculated*		*Observed*		*References*
(A = anthraquinone)	ν, cm^{-1} $\times 10^{-3}$	I[a]	ν, cm^{-1} $\times 10^{-3}$	I[a]	
1,4-$(NH_2)_2$-A	28.76	0.14	Not observed		
1,4-$(NH_2)_2$-$A \times 6$ H_2O supermolecule	28.51	0.10			
1,4-$(NHMe)_2$-A	28.66	0.19	Not observed		
1,4-$(NHCH_2Ph)_2$-A	29.19	0.30	26.49	0.14	29[b]
1-$NH_2$4-NHPh-A[c]	28.43	0.30	26.67	0.20	4
1,4-$(NHPh)_2$-A[d] 90/0	29.04	0.26	26.67	0.16	2[e]
80/0	28.89	0.28			
65/0	28.44	0.37			
50/5	28.02	0.46	25.13	0.39	4
40/10	28.03	0.56			
25/25	27.93	0.57			
25/25[f]	27.30	0.70			
1,4-[NH(2-styryl)]$_2$-A[c]	27.92	0.57	23.53	1.25	5
1,4-$(NHPh)_2$-5-NO_2-8-OH-A[c]	27.82	0.44	25.38	0.36	7
1,4-{NH[(4-COH)phenyl]}$_2$-5-NO_2-8-OH-A[c]	27.84	0.49	23.47	0.78	7[g]
1,4-{NH[(4-NO_2)phenyl]}$_2$-A[c]	27.79	0.67			
1-[NH(mesityl)]-4-{NH[(4-NO_2)-phenyl]}-}A[c]	28.36	0.53	23.26	1.20	5
	26.23	0.59			

[a] For calculated spectra is defined as the ratio of oscillator strengths of the 'blue' and 'red' transitions, for experimental—as the ratio of corresponding molar extinctions ε.
[b] Data for 1,4-bis[(1-phenyl-ethyl)amino]anthraquinone.
[c] For arylamino groups (except of mesityl) $\phi = 10°$, $\psi = 40°$.
[d] Calculations for various ψ/ϕ.
[e] Data for 1,4-bis(mesitylamino)anthraquinone.
[f] Amino group constrained to be planar; otherwise amino H atoms were placed in the plane of anthraquinone moiety.
[g] Data for 4-COPh derivative.

for both transitions (relative intensity of the second one ranges from 0.16 to 0.30) depending on the conformation adopted by the (1-phenylethyl)-amino group, whereas the transition energies remain essentially unchanged. This effect is not reproducible with 'pure' alkyl substituents and we have thus supposed that these changes are due to the direct interactions between phenyl rings and the anthraquinone π-system.

The calculations reproduce accurately that if the ψ angle decreases, the 'blue' band is shifted to longer wavelengths and its intensity increases, but the magnitude of these changes is obviously underestimated. It is conceivable

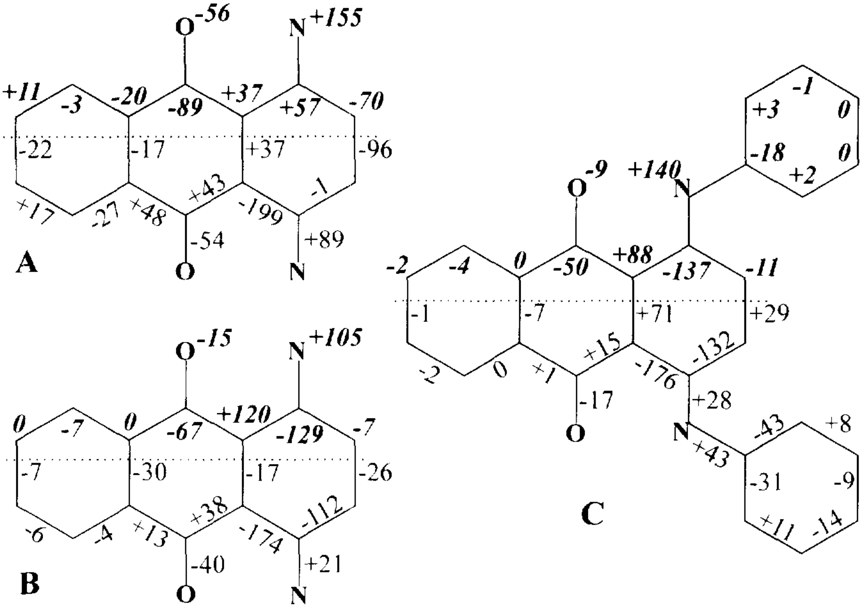


Fig. 2. Changes induced by excitation in atomic charges (at the top, $\times 10^3$) and bond orders (at the bottom, $\times$ 10^3) calculated on the INDO level for 1,4-diaminoanthraquinone (**A**— the first transition, **B**—the second one) and for 1,4-bisanilinoanthraquinone (**C**—the second transition).

that the second transition in 1,4-bis(alkylamino)anthraquinones is weaker and is more shifted hypsochromically than the calculations predict; this band is thus overlapped with the strong $\pi\pi^*$ anthraquinone transitions above 30 000 cm^{-1}.

For a hypothetical molecule with $\phi = \psi = 0°$, where the β positions are linked by methylene groups to the *ortho* positions of phenyls, a significant bathochromic shift without any considerable changes in the intensity has been predicted. The calculations strongly underestimate the spectral changes caused by the extension of aryl groups π-systems, as for instance, in *p*-styryl and *p*-nitrophenyl derivatives.

The reflection spectra of crystalline **I** and **II** given in Fig. 3 reveal two noticeable points, viz,

1. All absorption maxima are significantly shifted bathochromically, while in solutions both compounds show only minor solvatochromic changes. The magnitude of the shift of the 'blue' maximum is the largest.
2. Relative to solutions, the 'blue' maximum in the spectrum of **II** increases drastically in intensity

One conceivable reason is the perturbation of molecular orbitals due to intermolecular interactions. However, we failed to reproduce these effects in our calculations. The other possible explanation has its base in the specific packing motif of **II**, viewed in Fig. 4. We must consider that the first and second transitions are polarized along the long and short molecular axes, respectively. All the long molecular axes form an angle of 14° with the

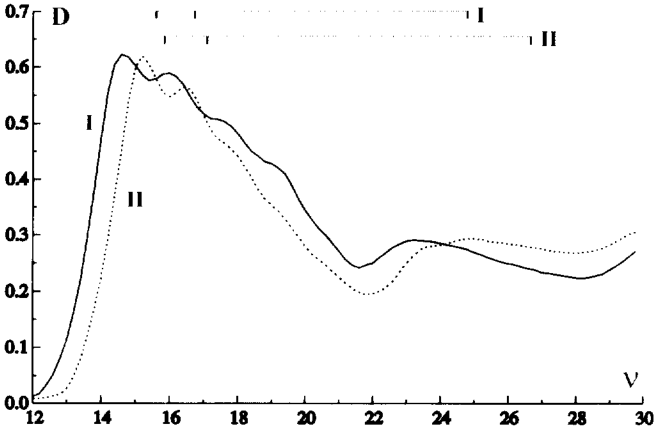


Fig. 3. Reflection spectra of crystalline 1,4-bisanilinoanthraquinone (**I**) and of 1,4-bis(mesitylamino)anthraquinone (**II**). The bars at the top of the diagram present the positions of absorption maxima of **I** and **II** in CCl_4 solutions.

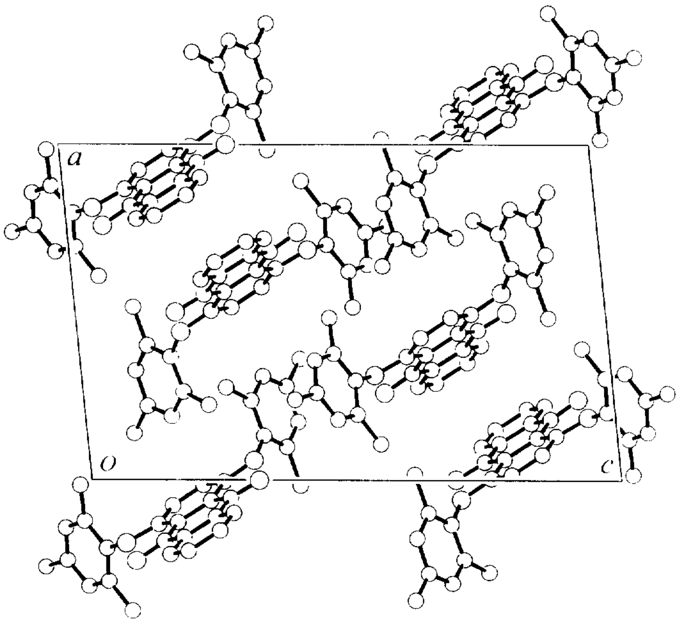


Fig. 4. Crystal packing diagram of 1,4-bis(mesitylamino)anthraquinone viewed down the *y* axis.

crystallographic *y* axis, whereas the short axes are coincident within 3° with the crystallographic [1 0 1] direction and thus the crystals ought to be pleochroic.

4 CONCLUSIONS

Calculations on the INDO/S level reproduce the general tendencies in the behaviour of the 'blue' absorption maxima, but strongly underestimate the magnitude of these changes. The effect of crystal packing results in the pronounced bathochromic shift of this maximum and, for the 1,4-bis(mesitylamino)anthraquinone, in the increase of its intensity.

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