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Relationship between π-Conjugation Size and Electronic Absorption Spectrum: Novel π-Conjugation Size Dependence of Indoaniline Dyes

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When the π-system at the quinone moiety in indoaniline dyes is expanded, the maximum absorption wavelength ($\lambda_{\max}$) of the main band in the absorption spectrum shows a shift to shorter wavelength (hypsochromic shift). This behavior stands in contrast to the generally accepted rule that expansion of a π-system leads to a bathochromic shift in the absorption spectrum, and the behavior was therefore investigated using the INDO/S method. It could be shown that the present systems are multicomponent systems, in which highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are located on different parts of the molecule. Therefore, only the LUMO rises in energy when the quinone system expands, thus leading to a widening of the HOMO−LUMO energy gap.

1. Introduction

The relationship between the size of the π-conjugated system and the UV−vis absorption spectrum provides an important guiding principle for the design of photofunctional materials. Since the color of the dye is mainly determined by its π-system, a number of both experimental and theoretical studies regarding the connection between π-systems and their electronic absorption spectra have been performed.[1] It is generally accepted that an increase in the size of the π-system causes a shift toward longer wavelength (bathochromic shift), and many molecules were designed based on this empirical rule. In many cases, this bathochromic shift has been explained by a decreasing gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. For example, in our theoretical comparison of UV−vis absorption spectra of naphthalene and perylene tetracarboxylic dianhydride derivative dyes, the bathochromic shift from the naphthalene to perylene dyes could be explained by the change in the HOMO−LUMO energy gap.[2]

One of the most important classes of cyan color dyes are the indoaniline dyes; their wide commercial applications include photography, dye diffusion thermal transfer (D2T2) print systems, and others.[3] Recently, they have also been applied as nonlinear optical materials,[4] because the origin of their chromophores is a strong donor−acceptor charge-transfer (CT) type electronic transition. Therefore, many papers were published in the past few years, including several theoretical studies[3,4e−h,5] aiming at the design of "high performance molecules". We already elucidated the electric absorption properties of the indoaniline dyes to obtain guiding principles for the molecular design.[3] In this context, we found that an increase of the dihedral angle between the quinone and aniline rings causes a bathochromic shift with decreasing absorption intensity. This novel relationship between molecular structure and absorption properties was also theoretically analyzed by molecular orbital (MO) calculations.[3a,b] Predictability of the absorption spectrum using MO calculations was also presented.[3c]

The relationship between the size of the π-system and the absorption spectrum is not yet well-known for the indoaniline dyes, and as far as we know, none of the research has been reported. However, 1,4-naphthoquinone type indoaniline dyes have been synthesized and the absorption wavelengths and intensities have been published.[6] Analysis of these data shows a surprising hypsochromic shift, that is, the maximum absorption wavelength ($\lambda_{\max}$) of the main band of 1,4-naphthoquinone type dyes is slightly shorter than that of the corresponding 1,4-benzoquinone type dyes (hypsochromic shift);[6h,i] however, this has not yet been discussed in the literature.[6] We were therefore interested in whether the observed hypsochromic shift continues to appear with further expansion of the π-system or whether it is an exceptional phenomenon, occurring only at the step from 1,4-benzoquinone to 1,4-naphthoquinone type dyes.

Among the next bigger class of the indoaniline dyes, the anthraquinone type dyes are almost unknown. Although 9,10-anthraquinone[7] and 1,4-anthraquinone[8] dyes were reported in a few papers and a patent, their absorption spectra remain unclear or are not known at all.

To elucidate the appearance and nature of the hypsochromic shift, we have synthesized 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ), 1,4-anthraquinone (1,4-AQ), and 9,10-anthraquinone (9,10-AQ) type indoaniline dyes with the same aniline moieties and recorded their absorption spectra. Analysis was backed by semi-empirical calculations of the absorption spectra, employing the INDO/S MO method,[9] after the equilibrium structures were determined at ab initio MO Hartree−Fock (HF) level.

2. Experimental Section

Preparation and Identification of Dyes. Synthesis of dyes **1a**,**b** has been reported earlier.[3c] Dyes **2a**−**4a** and **2b**−**4b** were prepared by oxidative condensation of suitable *p*-phenylenediamines and naphthol or anthrols using ammonium persulfate as oxidant, employing the previously reported procedure.[3b,c]

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TABLE 1: Observed and Calculated Absorption Spectra of Indoaniline Dyes

	acetonitrile solution[a]		cyclohexane solution[a]			calculation (INDO/S)			
dye	λ_{max} (nm)	ϵ_{max} (L/mol cm)	λ_{max} (nm)	ϵ_{max} (L/mol cm)	dihedral angle[b] θ (deg)	λ_{max} (nm)	f[c]	μ_{gr}[d] (debye)	μ_{ex}[e] (debye)
la	596	23 500	561	18 500	40.7	473.7	0.233	6.89	16.43
2a	589	17 400	563	15 400	44.7	459.4	0.170	5.41	13.54
3a	588	10 800	566	11 600	45.9	447.5	0.196	4.78	13.13
4a	558	7 500	539	7 500	51.5	453.8	0.110	4.96	15.30
1b	615	24 900	581	19 900					
2b	607	16 400	582	14 700					
3b	605	12 400	582	10 600					
4b	571	5 700	557	5 700					

[a] Concentrations of dyes are 10^{-4}−10^{-5} mol/L. [b] Optimized by HF/3-21G method. [c] Oscillator strength. [d] Ground-state dipole moment. [e] Excited-state dipole moment.

All dyes were purified by column chromatography until they gave a single spot on a thin layer chromatographic plate.

Identification of the dyes was carried out by the usual methods. The melting points are uncorrected.

4-[[4-(Diethylamino)phenyl]imino]-1(4H)-naphthalenone. **(2a).** Mp 118−119 °C; mass spectrum, *m/e* 304 (M^+), 289 (M^+-CH_3). Anal. Calcd for $C_{20}H_{20}N_2O_1$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.65; H, 6.62; N, 9.06. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.22 (t, 6H, J = 7.0 Hz), 3.42 (q, 4H, J = 7.0 Hz), 6.68−6.76 (m, 3H), 6.98−7.04 (m, 2H), 7.53 (d, 1H, J = 10.5 Hz), 7.58−7.73 (m, 2H), 8.17 (dd, 1H, J = 7.6, 1.6 Hz), 8.51 (dd, 1H, J = 7.6, 1.6 Hz).

4-[[4-(Diethylamino)-2-methylphenyl]imino]-1(4H)-naphthalenone. **(2b).** Mp 115−116 °C; mass spectrum, *m/e* 318 (M^+), 303 (M^+-CH_3). Anal. Calcd for $C_{21}H_{22}N_2O_1$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.37; H, 7.00; N, 8.82. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.21 (t, 6H, J = 7.0 Hz), 2.37 (s, 3H), 3.41 (q, 4H, J = 7.0 Hz), 6.53 (dd, 1H, J = 8.9, 3.0 Hz), 6.63−6.71 (m, 3H), 7.49 (d, 1H, J = 10.0 Hz), 7.58−7.73 (m, 2H), 8.18 (dd, 1H, J = 7.8, 1.4 Hz), 8.55 (dd, 1H, J = 7.8, 1.4 Hz).

4-[[4-(Diethylamino)phenyl]imino]-1(4H)-anthracenone. **(3a).** Mp 128−129 °C; mass spectrum, *m/e* 354 (M^+), 339 (M^+-CH_3). Anal. Calcd for $C_{24}H_{22}N_2O_1$: C, 81.33; H, 6.26; N, 7.90. Found: C, 81.7; H, 6.5; N, 7.6. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.23 (t, 6H, J = 7.0 Hz), 3.43 (q, 4H, J = 7.0 Hz), 6.73−6.81 (m, 3H), 7.03 (d, 2H, J = 8.9 Hz), 7.60−7.64 (m, 3H), 8.05 (dd, 2H, J = 8.6, 1.9 Hz), 8.73 (s, 1H), 9.00 (s, 1H).

4-[[4-(Diethylamino)-2-methylphenyl]imino]-1(4H)-anthracenone. **(3b).** Mp 147−148 °C; mass spectum, *m/e* 368 (M^+), 353 (M^+-CH_3). Anal. Calcd for $C_{25}H_{24}N_2O_1$: C, 81.49; H, 6.57; N, 7.60. Found: C, 82.0; H, 6.9; N, 7.4. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.22 (t, 6H, J = 7.0 Hz), 2.35 (s, 3H), 3.41 (q, 4H, J = 7.0 Hz), 6.60 (dd, 1H, J = 8.4, 2.7 Hz), 6.65−6.76 (m, 3H), 7.53−7.65 (m, 3H), 8.05 (dd, 2H, J = 8.6, 1.9 Hz), 8.74 (s, 1H), 9.02 (s, 1H).

10-[[4-(Diethylamino)phenyl]imino]-9(10H)-anthracenone. **(4a).** Mp 102−103 °C; mass spectrum, *m/e* 354 (M^+), 339 (M^+-CH_3). Anal. Calcd for $C_{24}H_{22}N_2O_1$: C, 81.33; H, 6.26; N, 7.90. Found: C, 81.69; H, 6.62; N, 7.76. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.18 (t, 6H, J = 7.0 Hz), 3.37 (q, 4H, J = 7.0 Hz), 6.68 (d, 2H, J = 9.2 Hz), 6.81 (d, 2H, J = 9.2 Hz), 7.31−7.70 (br m, 5H), 8.27 (br t, 2H), 8.50 (br d, 1H).

10-[[4-(Diethylamino)-2-methylphenyl]imino]-9(10H)-anthracenone. **(4b).** Mp 122−123 °C; mass spectrum, *m/e* 368 (M^+), 353 (M^+-CH_3). Anal. Calcd for $C_{25}H_{24}N_2O_1$: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.6; H, 6.8; N, 7.8. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.18 (t, 6H, J = 7.0 Hz), 2.29 (s, 3H), 3.35 (q, 4H, J = 7.0 Hz), 6.39−6.48 (m, 2H), 6.67 (s, 1H), 7.31−7.71 (br m, 5H), 8.29 (br t, 2H), 8.55 (br d, 1H).

Spectroscopic Measurements. The samples were dissolved in spectroscopic grade solvents (Kishida Chemical Co. Ltd.) and examined using a Hitachi automatic recording spectrophotometer (U-3400).

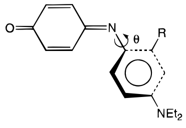
3. Calculation Method

We analyzed the absorption spectra of dyes **1a**−**4a** by MO calculation. In the first step, the molecular structures of the dyes **1a**−**4a** and the corresponding parent quinones (1,4-benzoquinone 1,4-naphthoquinone, 1,4-anthraquinone, and 9,10-anthraquinone) were optimized at HF/3-21G level using the Gaussian program package.[10] All structures were verified by frequency calculations to be minima on the potential energy surface.

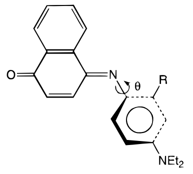
The equilibrium structures were then employed in a second step to calculate the absorption spectra by the INDO/S method.[9] In this method, which is a modified INDO version for absorption spectrum calculation, integrals are evaluated with the Nishimoto−Mataga formula[11] and the SCF calculations were executed at the closed shell HF level (RHF). Configuration interaction (CI) calculations were performed including single excited configurations from the ground state, consisting of 14 (occupied orbitals) × 14 (virtual orbitals) configurations.[12]

4. Results and Discussion

A. Relationship between Quinone Size and Absorption Spectrum. As shown in Table 1, the observed λ_{max} of the main band shifts to shorter wavelength (hypsochromic shift) with expansion of the π-conjugated system for each series (**1a**−**4a**, *N,N*-diethylaniline; **1b**−**4b**, 3-methyl-*N,N*-diethylaniline) in acetonitrile, and remains almost unchanged in cyclohexane.



1a R = H
1b R = Me



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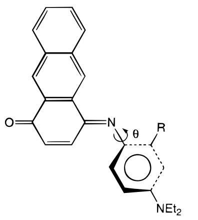
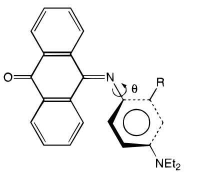


3a R = H
3b R = Me



4a R = H
4b R = Me

TABLE 2: Calculated Transition Properties of Indoaniline Dyes (INDO/S)

dye	transition energy[a] (cm^{-1})	transition property[b]	$^1E_{i\to j}$[c] (cm^{-1})
1a	21 110	0.729{(HOMO,49) → (LUMO,50)}	25780
		0.527{$(46)^d$ → LUMO}	31080
2a	21 770	−0.682{(HOMO,58) → (LUMO,59)}	26930
		0.504{$(54)^e$ → LUMO}	36730
		0.297{$(53)^f$ → LUMO}	36290
3a	22 350	0.685{(HOMO,67) → (LUMO,68)}	27500
		0.448{$(62)^f$ → LUMO}	36200
		−0.328{$(63)^e$ → LUMO}	41750
4a	22 040	−0.727{(HOMO,67) → (LUMO,68)}	28060
		−0.329{HOMO → (LUMO + 1)}	36580
		0.255{$(61)^f$ → LUMO}	40300

[a] Energy expression of λ_{max}. [b] Excitations having the CI coefficient over 0.25 are shown. [c] Orbital $i \to j$ singlet excitation energy. [d] Imino N lone-pair and quinone O lone-pair orbitals. [e] Imino N lone-pair orbital. [f] Quinone O lone-pair orbital.

Our results for the 1,4-benzoquinone and 1,4-naphthoquinone type dyes thus exactly reproduce the results of earlier studies,[6d,h,i] showing also that the trend continues for further extended systems like anthraquinone, which have been never reported before. The reason for this behavior, which is contrary to the generally accepted rule that expansion of the π-system causes a bathochromic shift, will be discussed in detail in section **4B**.

Table 1 also shows that λ_{max} values of the 3-methyl-substituted aniline type dyes (**1b**−**4b**) appear at longer wavelength (~20 nm) compared to those of the corresponding nonsubstituted dyes (**1a**−**4a**). This bathochromic shift can be readily explained by the substituent effect of the methyl group and was reported earlier.[3b]

B. Reason of the Hypsochromic Shift. The reason for the unexpected hypsochromic shift was sought after by calculation of the absorption spectra using semiempirical MO methods and analysis of the molecular orbitals (see chapter 3). As seen in Table 1, the calculated spectra agree with the experimental trend of a shift toward shorter wavelengths with expansion of the π-system,[13] although the order for the two isomers of the anthraquinone type dyes could not be reproduced. We will therefore restrict our discussion on dyes **1a**−**3a** in this section and analyze the difference of **3a** and **4a** in section **4D**.

Following the already mentioned principle that a change in the dihedral angle can cause a shift in λ_{max},[3a,b] we looked for the structural difference between the molecules. However, the dihedral angle was found to increase slightly with expansion of the quinone system (Table 1), which should lead to a bathochromic rather than the observed hypsochromic shift. Therefore, the experimentally observed shift cannot be explained by structural differences, but has to have its reason in the different electronic structure of the dyes.

Analysis of the CI components of the transition (Table 2) showed that the transition can be roughly described by a HOMO → LUMO CT type excitation with only small contribution of the n-π^* excitations (see Figure 1).[14] It is therefore justified to restrict the following discussions to the properties of HOMO and LUMO and the excitation between them.

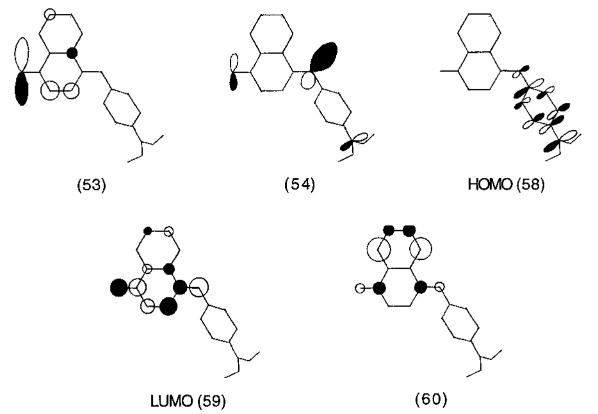


Figure 1. Frontier molecular orbitals of indoaniline dye (**2a**) (INDO/S).

The singlet HOMO → LUMO excitation energy ($^1E_{HOMO\to LUMO}$, Table 2) is further split up according to eq 1 (Table 3)

$$^1E_{HOMO\to LUMO} = \Delta\epsilon_{HOMO,LUMO} - J_{HOMO,LUMO} + 2K_{HOMO,LUMO} \quad (1)$$

($\Delta\epsilon$, HOMO−LUMO energy gap; J, Coulomb integral; K; exchange integral) for the dyes **1a**−**3a.** It thus becomes clear that, because the electronic interaction term ($J - 2K$) remains almost constant with the expanding quinone π-systems, the excitation energy $^1E_{HOMO\to LUMO}$ increases by almost the same amount as the HOMO−LUMO energy gap widens.

Figure 2 shows that the orbital phases and energies of the HOMOs, which are almost entirely localized at the aniline ring, are almost the same for dyes **1a**−**3a** (same aniline moiety). On the other hand, it can be seen that the energy levels for the LUMO, localized at the quinone moiety, rise with expanding π-system and thus cause the increase in the HOMO−LUMO energy gap.

A comparison of the orbital energies and the patterns of the LUMOs of dyes **1a**−**4a** with those of the parent quinones revealed a very close similarity (Figure 2). The donor (HOMO) and acceptor (LUMO) parts of the indoaniline dye can thus be seen as nearly independent systems, which is one of the important properties of the CT type chromophores. In other words, the hypsochromic shift results from the change in the electronic structures of the acceptor moiety (parent quinones, see section **4C**).

A further possibility to discuss the hypsochromic shift is the change of the dipole moment of the excited state, which is connected with the electron affinity (ϵ_{EA}) of the acceptor moiety. The decrease of the dipole moment in the order **1a** > **2a** > **3a** is thus synonymous with a decreasing electron affinity in the quinone moiety, when the π-system expands. Using Koopman's theorem ($\epsilon_{EA} = -\epsilon_{LUMO}$) and the fact that the energy of the HOMO is not much influenced by the change of the quinone moiety, we can thus show that the decrease in the dipole moment

TABLE 3: Detail of HOMO → LUMO Excitation Properties of Indoaniline Dyes (INDO/S)

dye	$^1E_{HOMO\to LUMO}$[a] (cm^{-1})	$\Delta\epsilon_{HOMO,LUMO}$[b] ($cm^{-1}$)	$J_{HOMO,LUMO}$[c] (cm^{-1})	$2K_{HOMO,LUMO}$[d] (cm^{-1})	$J - 2K$ (cm^{-1})
1a	25 780	47 190	25 370	3 960	21 410
2a	26 930	48 160	24 050	2 820	21 230
3a	27 500	48 500	23 460	2 460	21 000
4a	28 060	49 050	22 430	1 440	20 990

[a] Singlet excitation energy. [b] Difference of orbital energies. [c] Coulomb integral. [d] Exchange integral.

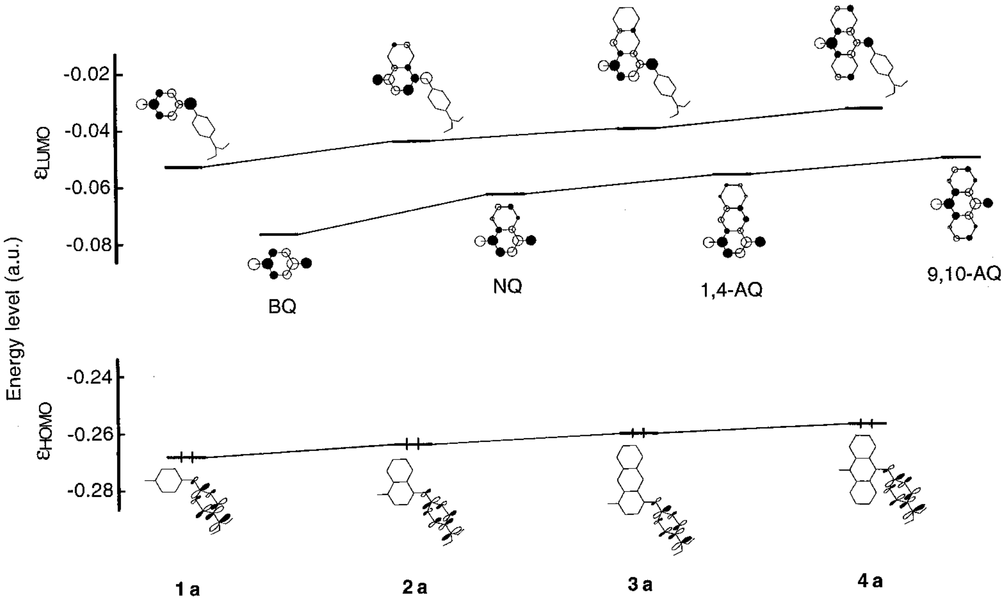


Figure 2. HOMO and LUMO energy diagram for indoaniline dyes (**1a**, **2a**, **3a**, and **4a**) and corresponding parent quinones (BQ, NQ, 1,4-AQ and 9,10-AQ) (INDO/S).

actually indicates the increase in the HOMO−LUMO gap (i.e., the hypsochromic shift).

C. Properties of the Parent Quinones. Studies of the *p*-quinones, focusing on the size of the π-system, were already reported both the experimentally and theoretically.[15] On the basis of the experimental results, it was shown that electrochemical reduction is easier in the order BQ> NQ > 1,4-AQ > 9,10-AQ and the order of electron affinity (acceptor strength) is the same.[15d,i,j] Therefore, the relative energies of LUMOs of this study are consistent with the observed results. HOMO and LUMO properties and the calculated absorption spectra of the parent quinones also agree very well with the previous calculations.[15g,h,i] Although the LUMO energy rises with increasing π-system, the energy of the highest occupied π-MO, delocalized over the molecule, rises even stronger and the energy difference decreases therefore. The lowest singlet $\pi-\pi^*$ transition shifts therefore toward longer wavelength (bathochromic shift).

The reason why the LUMO shifts to higher energy with expansion of the π-system can be explained from the character of the orbital. At a first glance, the LUMOs of NQ, 1,4-AQ, and 9,10-AQ are all strongly localized at the benzoquinone part and only small contributions can be seen at the extended parts (Figure 2). However, if we look at the orbital phases, it becomes clear that between the core part (benzoquinone) and the extensions new nodal planes appear (two for NQ, four for 1,4-AQ and 9,10-AQ). This means that the antibonding character of the LUMO increases with the extension of the π-system, which causes the orbital energy to rise. Comparing the LUMOs of both AQ isomers, the antibonding interaction in the 9,10-AQ is larger than in the 1,4-AQ (Figure 2), therefore, the 9,-10-AQ LUMO energy is higher.

D. Isomers of Anthraquinone Type Dyes. The two isomer dyes **3a** (1,4-anthraquinone type) and **4a** (9,10-anthraquinone type) were found to have different λ_{max} and intensities, despite the fact that their π-systems are equivalent in size. Surprisingly, our calculations could not reproduce the experimental shift to shorter wavelength, although the oscillator strengths are consistent with the experimental intensities (Table 1). Analysis of the CI wavefunction and the particular excitation energies revealed that the HOMO → LUMO excitation, which is dominant in the CI expansion for both **3a** and **4a**, shows the correct behavior (i.e., shifts to shorter wavelength from **3a** to **4a** (Table 2)). However, it also became apparent that the HOMO → (LUMO + 1) excitation, which contributed less than 4% in **1a**−**3a**, becomes the second strongest contribution in the expansion for **4a** with about 11%. Thus, the calculated smaller transition energy for **4a** results from the stronger contribution of the HOMO → (LUMO + 1) excitation to the CI wavefunction.[16]

Provided this difference in the CI expansions for **3a** and **4a** is no artifact, the failure to reproduce the experimental results is probably due to the limitation of the INDO/S method with truncated CI expansion.[17]

5. Summary

In the previous sections, we have reported investigations regarding the hypsochromic shift in a series of indoaniline dyes with expanding π-system. This finding is in contrast to the rule that both the expansion of the π-system and the increase of the dihedral angle between the aniline and quinone rings generally lead to a bathochromic shift of λ_{max} in the absorption spectrum.

Molecular orbital analysis showed that the investigated molecules are multicomponent systems (i.e. the HOMO is localized at the aniline moiety, whereas the LUMO is localized at the quinone moiety, strongly resembling the LUMO of the parent quinone). It is thus obvious that a change in the π-system of the quinone moiety would mainly affect the LUMO, but will influence neither energy nor character of the HOMO. Because in our systems the LUMO has antibonding character, which becomes more pronounced with expansion of the π-system, the energy of the LUMO increases in the order **1a** < **2a** < **3a**. As a result, the energy difference $\Delta\epsilon_{HOMO,LUMO}$, which can be seen as a measure for the transition energy in a first order approximation, also increases in the same order and is then detected as the hypsochrornic shift in the absorption spectrum.

For dye **4a** (9,10-anthraquinone type), this approximation does not hold anymore, (i.e., although $\Delta\epsilon_{HOMO,LUMO}$ continues to increase with **4a**, the transition energy falls back behind the value for dye **3a** (1,4-anthraquinone type)). The reason for this behavior lies in the stronger mixing of the HOMO → (LUMO + 1) excitation into the CI wavefunction, which leads to the decrease in the transition energy (CI effect).

Although the previous findings, taken together, look like a counter example to the generally accepted rule, that enlargement of a π-system causes a bathochromic shift, we have to be aware of the fundamental difference of the investigated systems compared with other molecules. For systems, for which the rule holds (e.g., the parent quinones), both HOMO and LUMO are localized at the same part of the molecule and therefore structural changes will affect both in the same way. On the other hand, in multicomponent systems with only weak interactions between the components like the ones presented here, HOMO and LUMO might be located at different moieties and a structural change in one of the moieties will then only affect one of the orbitals but leaves the other one more or less undisturbed. We conclude that the absorption spectrum of multicomponent chromophores (e.g., donor−acceptor CT type dyes) cannot be simply explained by general rules based on simple π-systems. Instead, it is necessary to consider not only the energy of the orbitals, but also their characters and combine these information.

As this study shows a typical example of the novel absorption spectrum shift and this analysis provides a good insight into its mechanism, which will be helpful for the future design of multicomponent chromophores.

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(12) Large CI size calculations (35 × 35, S-CI) were also performed to evaluate the CI effect, but the results were almost the same as by the 14 × 14 S-CI calculations. Therefore, we adopted the 14 × 14 S-CI calculation for this study.

(13) In some cases, INDO/S calculation underestimates the absorption wavelength, especially for the organic dyes and pigments. We have previously proposed the relationship between the observed and calculated λ_{max} (ref 17); λ_{max} (obs) = 1.65 λ_{max} (calcd) −187 (nm). The scaled values are 595 nm (**1a**), 571 nm (**2a**), 551 nm (**3a**), and 562 nm (**4a**).

(14) The next dominant elements are roughly described as (imino N atom lone-pair orbital) → LUMO excitation and (quinone O atom lone-pair orbital) → LUMO excitation (Table 2 and Figure 1). Contribution of these excitations for the transition are almost the same (∼30%) for dyes **1a**, **2a**, and **3a**. Expanding the π-system of the quinone ring, these excitation energies are increasing. These changes in the excitation energies can only be explained by a decreasing electronic interaction term ($J - 2K$), but not by a widening energy gap ($\Delta\epsilon$). The reason is that following the expanding π-system of the quinone ring, the quinone orbitals become more diffuse and the Coulomb integral (J) decreases.

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(16) To consider the influence of the dihedral angel between the quinone and aniline rings, the dihedral angle of dye **3a** was adjusted to 50.6° (almost same value as dye **4a**). However, λ_{max} changes only by 2.4 nm (**3a** with 50.6°: λ_{max} 449.9 nm, f 0.175). We conclude therefore, that the calculated longer λ_{max} for **4a** is unlikely to be the result of an error in the geometry optimization, but originates from differences in the electronic structure.

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