The Relationship between the Structures and Absorption Spectra of Cyan Color Indoaniline Dyes

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The absorption spectra of 23 indoaniline dyes were calculated on the AM1-optimized structures by means of the INDO/S method. The observed and calculated absorption wavelengths showed good correlation for the main (longest wavelength) absorption bands (observed at 560–670 nm), and there was fair correlation between the observed molar extinction coefficients and the calculated oscillator strengths. The observed absorption wavelengths could be reproduced by the calculation for the subabsorption bands near the visible region (observed at 320–380 nm). A qualitative correlation of the solvatochromic shift with the difference between ground and excited state dipole moments was obtained.

Introduction

We have previously reported a surprising, novel relationship between the structures and the absorption spectra of azomethine dyes: An increase in the dihedral angle between the quinone ring and the aniline ring leads to an increase in the absorption wavelength despite the lower planarity and reduced π-conjugation.[1] This bathochromic shift has been explained by CI; i.e., mixing between HOMO → LUMO (π–π*) and imino N lone pair → LUMO (n–π*) configurations.

Indoaniline dyes are cyan colar dyes that are widely used as photographic materials,[2] a dye diffusion thermal transfer (D2T2) system,[3] and other color materials where the absorption spectrum design is of crucial importance. Investigations of the effects of substituents on the absorption spectra of indoaniline dyes were reported first by Vittum and Brown et al.[4] about 50 years ago and more recently by Issa et al.[5] and Panchártek.[6] The solvatochromic effect was also studied a half century ago by Brooker and Sprague, who measured the phenol blue absorption spectrum in four different solvents.[7] Figures reported on the hydrogen bonding and solvent effects in phenol blue and its derivatives.[8] In addition, Smith's analyses using HMO and anti-symmetrized molecular orbital (ASMO) CI calculations for indoaniline dyes showed qualitative substituent effects.[9] Hofmann et al. used CNDO/2 and Pariser–Parr–Pople PPP-CI calculations to determine the molecular structures and absorption spectra, respectively, of azomethine dyes (including phenol blue).[10] Recently, Yue et al. calculated the effects of substituents on the absorption wavelength of indoaniline dyes using the PPP-CI method,[11] and Tokita et al. calculated the substituent effects for indoaniline dyes using PPP-CI and INDO/S methods.[12] Neither the absorption intensities nor the subabsorption bands were considered in detail in these works.

Cyan color dyes are characterized an absorption maximum (λ_{max}) near 650 nm with a large absorption intensity. Moreover, the other absorption bands should not appear in the visible region. MO calculations of the absorption spectra of cyan dyes offer useful information for the design and synthesis of new dyes. Although the λ_{max} can be determined empirically, predicting the intensity of λ_{max} and the subabsorption band spectrum is very difficult without the aid of MO calculations.

The absorption spectrum calculations are usually done by the PPP method.[13] A recent report by Nishimoto indicates the potential power of the PPP method even for subabsorption band calculations when the random phase approximation (RPA) is used.[14] Since the PPP method was originally designed for π-electron systems, its application to nonplanar molecules and n–π* transitions is difficult. As was reported previously,[1a] the degree of nonplanarity and the absorption spectra of indoaniline dyes are closely related. Therefore, all valence electrons must be considered. For this reason, we chose the INDO/S method[15] for the absorption spectra calculations. We have already tested the validity of the INDO/S method by comparing the observed and calculated absorption spectra for various organic dyes,[16a] near-IR-absorbing inorganic

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Table I. Calculated and Observed Absorption Data for Dye 1

observed[a]		calculated (INDO/S)[b]			
λ_{max} (nm)	ε (L/mol cm)	λ_{max} (nm)	f[d]		transition character[c]
590	26500	493.5	0.423	−0.861	{(HOMO,60)→(LUMO,61)}
				−0.365	{(56)→(61)}
		439.9	0.007	+0.650	{(55)→(61)}
				+0.472	{(54)→(61)}
373	7200	362.0	0.326	+0.661	{(59)→(61)}
				−0.388	{(56)→(61)}
				−0.339	{(57)→(61)}
				+0.335	{(53)→(61)}
		337.1	0.070		

[a] Cyclohexane solution (~10^{-5} mol/L). [b] CI size 14×14. [c] {(a)→(b)} represents a configuration a→b. Coefficients greater than 0.3 are shown. [d] Oscillator strength.

dyes,[16b] and naphthoquinone methide dyes.[1b] Good correlations were obtained. The possibility for obtaining very precise correlations for dyes of the same type has also been demonstrated.[1b] The indoaniline dye absorption spectrum depends on the dihedral angle between the quinone and the aniline rings.[1] Consequently the molecular geometry for the calculation must be chosen very carefully.

In this paper, the observed and calculated absorption spectra of 23 indoaniline dyes are presented, and the relationships between the observed and calculated spectra allow the prediction of the absorption spectrum of a new dye. The AM1 (Austin Model 1)[17]-optimized molecular structures were used for the INDO/S[15] calculations of the λ_{max}, the oscillator strength, and the dipole moments of the ground states as well as the excited states.

Solvent effects are also interesting and important, although the mechanism is not well understood. We have examined the solvatochromic shift by evaluating the difference between the ground and excited state dipole moments according to Ooshika's method.[18]

Results and Discussion

(i) Relationship between Structure and Absorption Spectra. The observed and calculated absorption spectra of 1 and the transition characters are shown in Table I. The orbitals appearing in the three lowest energy transitions of the important configuration of 1 are shown in Figure 1. The transition corresponding to the longest wavelength (main) absorption band (S_1) is mainly of HOMO (aniline ring) → LUMO (quinone ring) charge-transfer character (see Table I and Figure 1). The second transition (S_2) exhibits a very weak oscillator strength in the calculation and was not observed experimentally. S_2 is largely of quinone O atom Py orbital→LUMO character. The subabsorption band observed next corresponds to the third transition (S_3) of the calculation. This transition mainly consists of a transition inside the quinone ring with a slight contribution from a transition on the aniline ring.

The relationship between the structure and the main absorption band is unusual. Increasing the dihedral angle between the quinone ring and the aniline ring (from 17° → 90°) shifts λ_{max} to a longer wavelength and decreases the oscillator strength (Figure 2), despite the decrease in planarity and π-conjugation resulting from the angle change. The change in the oscillator strength can be explained by a decrease in the overlap of the wave functions of the ground state and the excited state (see Figure 1). However, a simple HOMO–LUMO energy gap argument cannot be used to explain the λ_{max} change. Remarkably enough, the configuration mixing of the imino N lone pair → LUMO and HOMO → LUMO transitions is the most important influence on λ_{max}. The second and the third transitions are relatively unaffected by the dihedral angle since they consist mainly of the quinone ring transitions. A detailed analysis of the wave function will be published

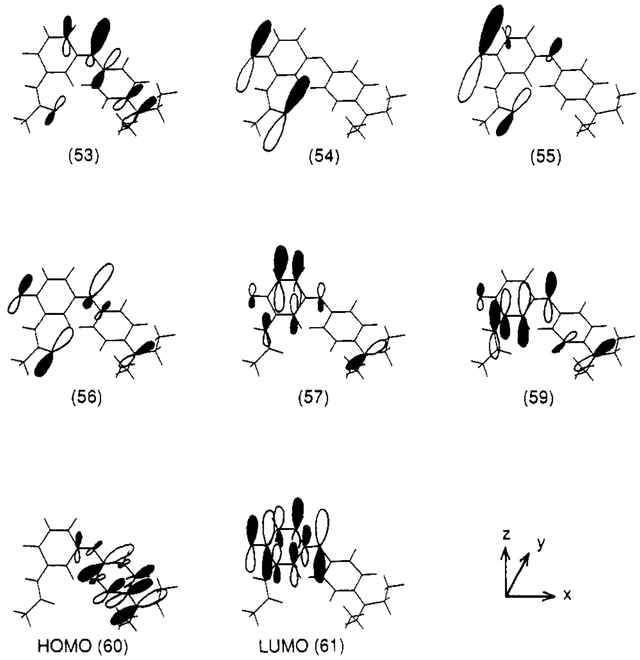

Figure 1. Molecular orbitals of the AM1-optimized structure of 1 (INDO/S).

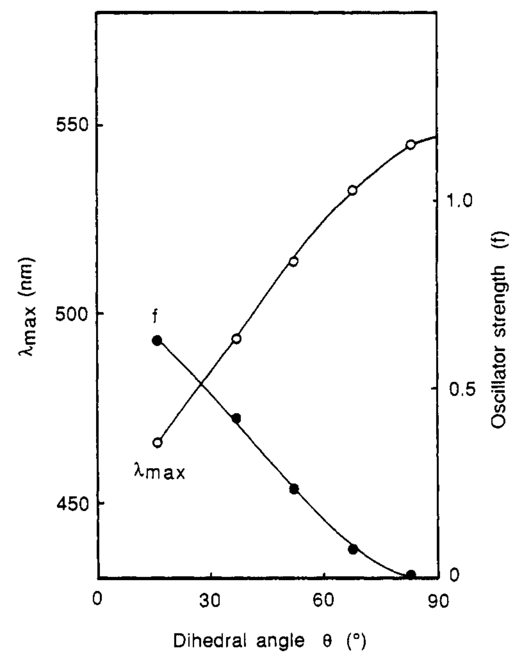

Figure 2. Changes in the spectrum of 1 caused by changes in the dihedral angle between the quinone and the aniline rings (INDO/S, CI: 14 × 14).

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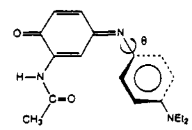
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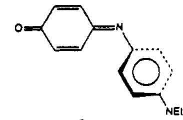
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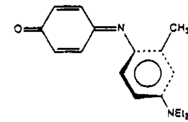
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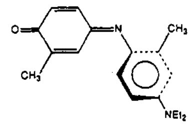
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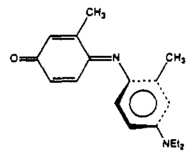
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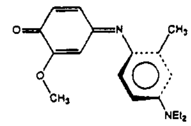
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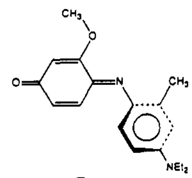
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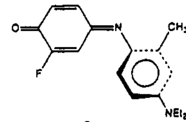
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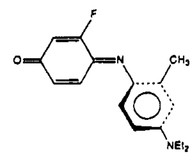
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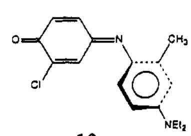
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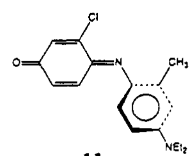
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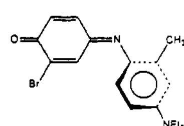
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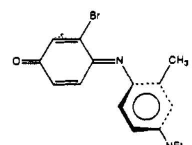
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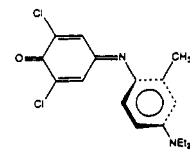
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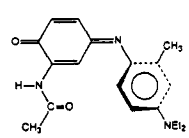
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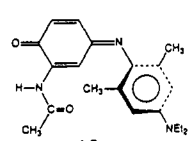
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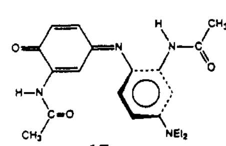
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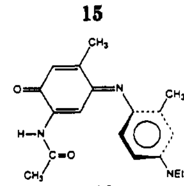
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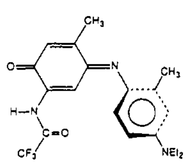
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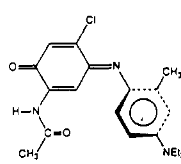
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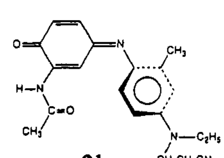
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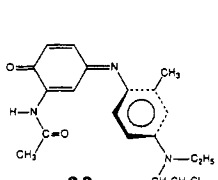
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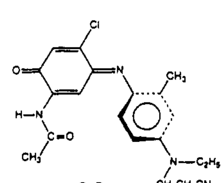
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elsewhere.[1a] In this paper, the main absorption band (S_1) and the subabsorption band (S_3) will be considered; the S_2 transition, which was not observed, will not be discussed.

(ii) Comparison of the Observed and Calculated Spectra. The observed and the calculated absorption spectra (for the main bands and the subabsorption bands) and the AM1-optimized dihedral angles[19] for dyes **1–23** are shown in Table II. The observed solvatochromic shift (ΔE_{max}; the difference between the transition energy measured in cyclohexane and that measured in acetonitrile) is shown in Table II together with the difference between the ground and the excited states dipole moments.

The relationships between the observed λ_{max} and the λ_{max} obtained from a 14 × 14 CI calculation are shown in Figures 3 and 4 for the main band and the subband, respectively. The relationships between the observed molar extinction coefficients (ϵ) and the calculated oscillator strengths (f) are shown in Figures 5 and 6 for the main band and the subband, respectively.

The correlation between the observed and the calculated λ_{max} of the main band is good (Figure 3). The correlation between the observed molar extinction coefficient and the calculated oscillator strength of the main band is fair

(19) The AM1-optimized geometries almost reproduced the X-ray structures (Osano, Y. T.; Matsuzaki, T.; Murata, Y., manuscript in preparation). The dihedral angles of **15** and **16** are 44.5° and 56.7°, respectively, in the X-ray structure.

Table II. Observed and Calculated Absorption Spectra of Indoaniline Dyes

	observed				calculated (INDO/S)					
					(CI: 14 × 14)[a]			(CI: ~1260 config)[a]		
molecule	λ_{max}[b] (nm)	ϵ ($\times10^{-4}$)[b] (L/mol cm)	ΔE_{max}[c] (cm^{-1})	dihedral angle (deg)[d]	λ_{max} (nm)	f[e]	$\Delta\mu$[f] (debye)	λ_{max} (nm)	f[e]	$\Delta\mu$[f] (debye)
1	590	2.65	720	37.3	493.5	0.423	12.17	500.9	0.414	11.85
	373	0.72			362.0	0.326		369.4	0.338	
2	561	1.85	1050	43.0	476.5	0.182	4.57[g]	482.2	0.239	7.55
					463.8	0.150	2.31			
	344	0.56			331.1	0.575		338.0	0.584	
3	581	1.99	950	44.5	483.5	0.274	10.14	490.3	0.289	10.91
	354	0.68			331.4	0.554		338.1	0.560	
4	577	1.76	910	43.4	477.5	0.302	11.28	485.9	0.303	11.51
	350	0.65			331.9	0.586		339.6	0.594	
5	577	1.62	990	42.8	476.9	0.211	7.50	484.0	0.221	8.05
	350	0.65			327.6	0.574		334.1	0.588	
6	572	1.44	1060	45.9	473.1	0.293	10.92	481.8	0.288	11.00
	340	0.69			330.5	0.544		338.5	0.568	
7	571	1.35	980	38.1	476.7	0.291	10.75	476.6	0.285	10.82
	340	0.68			329.1	0.545		336.1	0.570	
8	596	2.20	1060	42.7	493.6	0.384	13.04	501.9	0.375	12.76
	350	0.64			336.5	0.539		343.4	0.541	
9	588	2.22	1030	39.5	489.6	0.355	12.22	498.1	0.346	11.96
	350	0.67			337.3	0.541		344.1	0.543	
10	603	2.48	1080	41.0	490.7	0.394	12.96	502.3	0.371	12.43
	360	0.67			333.3	0.517		344.3	0.529	
11	604	1.85	980	40.5	490.3	0.362	12.58	501.8	0.340	12.05
	360	0.59			332.9	0.528		342.9	0.537	
12	605	2.52	1120	38.4	483.0	0.411	12.88	495.5	0.383	12.25
	360	0.70			331.4	0.515		344.9	0.522	
13	607	1.51	970	39.2	485.9	0.368	12.64	497.9	0.341	11.97
	365	0.48			330.7	0.530		342.6	0.532	
14	628	3.08	1170	36.0	491.4	0.451	13.28	504.7	0.422	12.67
	363	0.73			335.1	0.498		348.7	0.501	
15	609	2.70	700	39.8	504.2	0.411	12.45	511.9	0.401	12.15
	378	0.76			361.8	0.345		368.5	0.353	
16	666	0.84	240	59.3	532.0	0.194	13.83	540.1	0.186	13.42
	369	0.57			352.3	0.288		358.8	0.325	
17	622	3.41	300	33.2	520.3	0.537	7.29	528.4	0.521	7.05
	363	0.48			364.5	0.314		372.5	0.337	
18	606	2.24	630	37.5	494.5	0.364	12.09	501.6	0.356	11.80
	374	0.73			364.5	0.195		370.3	0.205	
19	628	2.79	660	37.2	505.7	0.373	11.33	513.1	0.363	11.05
	380	0.70			354.6	0.303		360.5	0.316	
20	634	2.52	640	34.5	512.9	0.460	11.05	521.7	0.440	10.68
	382	0.66			367.6	0.269		376.5	0.298	
21	583	1.25	680	40.3	492.3	0.409	5.73	501.2	0.389	5.38
	364	0.53			357.5	0.284		366.0	0.333	
22	593	1.41	600	40.4	495.5	0.407	8.57	504.6	0.390	8.20
	364	0.52			357.8	0.291		367.0	0.336	
23	605	1.86	810	34.9	500.5	0.457	5.66	509.8	0.429	5.35
	379	0.64			364.3	0.226		373.1	0.283	

[a] See text. [b] Cyclohexane solution (10^{-4}–10^{-5} mol/L). [c] $\Delta E_{max} = E_{max}$ (in cyclohexane) − E_{max} (in acetonitrile). (E_{max} = Transition energy). [d] Optimized by AM1 method. [e] Oscillator strength. [f] $\Delta\mu = \mu$ (excited state) − μ (ground state). (μ = Dipole moment). [g] Two INDO/S calculated transitions are assigned to the observed main absorption band. The HOMO → LUMO transition and the quinone O atom Py orbital → LUMO transition are in accidental degeneracy, therefore both characters are mixed. In the figures, the λ_{max} value is the simple average of two states, the oscillator strength is the sum of two states, and no value is plotted in Figure 9.

(Figure 5) but not as good as the correlation for λ_{max}. The observed molar extinction coefficient and the calculated oscillator strength are, in general, not strictly proportional because the oscillator strength represents the integral over one absorption band. Since the observed shapes of the first absorption bands for all the molecules in this indoaniline dye series are almost the same, the comparison is considered to be meaningful.[20]

The correlation between the observed and the calculated λ_{max} of the subabsorption band (Figure 4) is poor. Although the calculated absolute value for each molecule is close to the observed one, the calculated wavelengths are separated into two groups. The first group, near 330 nm, corresponds to the group of molecules without the $NHCOCH_3$ group in the quinone ring. The second, near 360 nm, corresponds to molecules with the $NHCOCH_3$ (or the $NHCOCF_3$) in the quinone ring. Since the subabsorption band consists mainly of the quinone transition, the longer λ_{max} of the group of molecules with the $NHCOCH_3$ group in the quinone is the result of the substituent effect. There is no correlation between the absorption intensity and the oscillator strength for the subabsorption band. The data fall into one of two groups depending on the presence or absence of the $NHCOCH_3$ group (Figure 6).

(iii) Effect of the CI Size on the Description of the Subband. In general, CI calculations have three major

(20) The relationship between the observed molar extinction coefficient and the observed oscillator strength for the main band was almost linear. Therefore, the relationship between the observed and the calculated oscillator strengths was almost the same as the relationship between the observed molar extinction coefficient and the calculated oscillator strength (Figure 5). For the subband, the spectral shape was not resolved because the band overlapped with other bands; therefore, the observed oscillator strength was not determined.

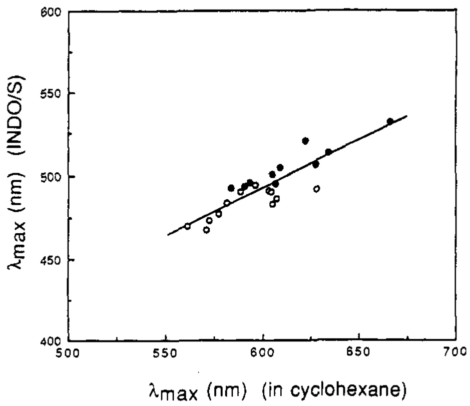

Figure 3. Relationship between the observed and the calculated absorption maximum (λ_{max}) of the main band. (CI: 14 × 14; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring. The line was determined by the least-squares method.)

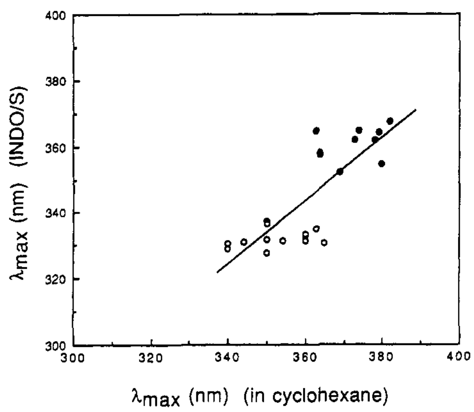

Figure 4. Relationship between the observed and the calculated absorption maximum (λ_{max}) of the subband. (CI: 14 × 14; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring. The line was determined by the least-squares method.)

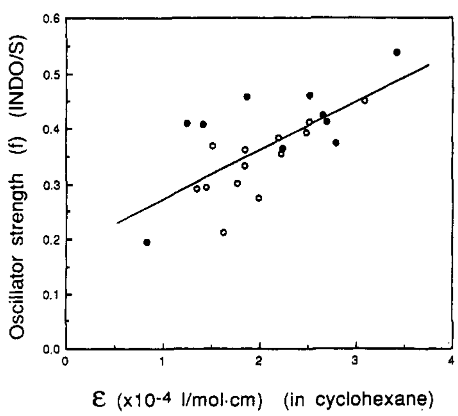

Figure 5. Relationship between the observed molar extinction coefficient (ϵ) and the calculated oscillator strength (f) of the main band. (CI: 14 × 14; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring. The line was determined by the least-squares method.)

problems: (1) they are limited by the CI size, (2) they do not take into account double or multi-electron excited configurations, and (3) they use only a single reference.

In this study we focused on the effect of the CI size. We used a 14 × 14 S-CI calculation for the results discussed so far and found that the absorption spectrum could be predicted with a fair level of accuracy. However, the

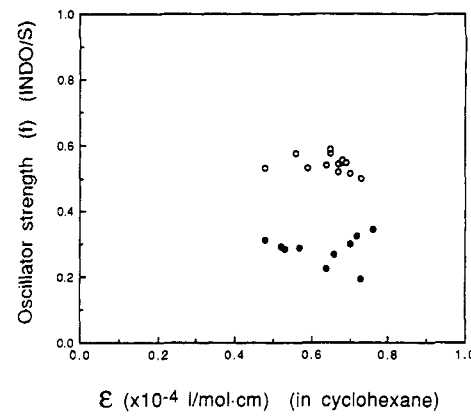

Figure 6. Relationship between the observed molar extinction coefficient (ϵ) and the calculated oscillator strength (f) of the subband. (CI: 14 × 14; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring.)

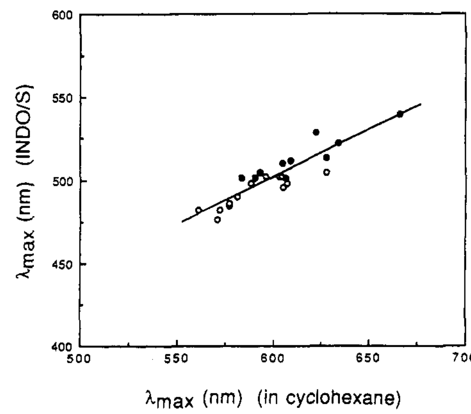

Figure 7. Relationship between the observed and the calculated absorption maximum (λ_{max}) of the main band. (CI: ~1260 config; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring. The line was determined by the least-squares method.)

subabsorption band properties (λ_{max} and intensity) were not predicted as accurately.

For the CI calculation, we used SCF orbitals. Although in the SCF process the occupied orbitals are optimized, the vacant orbitals are not. In principle, all vacant orbitals should be considered. Therefore, we carried out nearly 1260 CI configuration calculations that included all vacant orbitals and the occupied orbitals for a net amount of 1260 (S-CI) configurations (referred to as ~1260 config hereafter).

The relationships between the observed and the calculated λ_{max} obtained with ~1260 config are shown in Figures 7 and 8 for the main band and the subband, respectively. As the CI size increases, the correlation between the observed and calculated λ_{max} is improved for both the main and the subabsorption bands. The improvement in the correlation for the subabsorption band is especially remarkable. At the 14 × 14 CI size (Figure 4), the calculated values completely separate into two groups. With ~1260 config, the calculated results become close to the observed values (Figure 8). Other spectroscopic properties do not change when the CI size is increased.

The improvement of the subabsorption band λ_{max} calculation when the larger S-CI size is used can be explained by the inclusion of the orbitals in the substituent group. That is, the subband consists of the transitions inside the quinone ring; and the vacant orbitals, which are

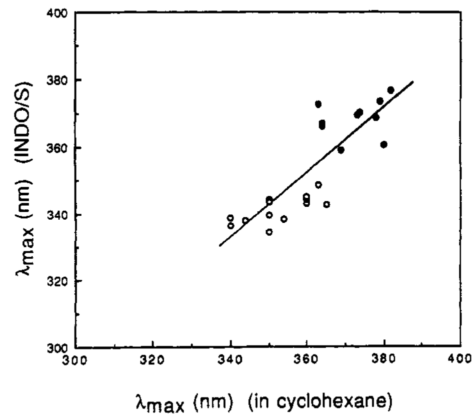

Figure 8. Relationship between the observed and the calculated absorption maximum (λ_{max}) of the subband. (CI: ~1260 config; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring. The line was determined by the least-squares method.)

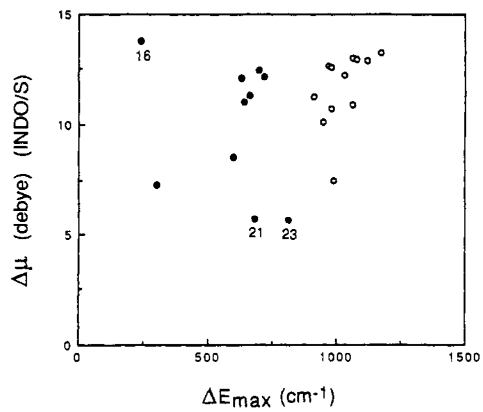

Figure 9. Relationship between the observed solvatochromic shift ($\Delta E_{max} = E_{max}$ (in cyclohexane) − E_{max} (in acetonitrile)) and the calculated dipole moment difference ($\Delta\mu = \mu$ (excited state) − μ (ground state)) of the main band. (CI: 14 × 14; (○) molecules without $NHCOCH_3$ in the quinone ring; (●) molecules with $NHCOCH_3(F_3)$ in the quinone ring.)

attributed to the substituent, lie in the high energy area of the vacant orbital space. As the CI size increases, these vacant spaces start to be taken into account. It should be noted that there exists a difficulty in calculating the higher excited states. The difficulty is mainly due to insufficient electron correlation.[21,22]

(iv) Solvent Effect. The solvatochromic shift has been an important subject of study. For example, the solvent effect on the absorption spectrum of phenol blue has recently been treated by the perturbation method (modification of the Hamiltonian).[23] Another approach to analyzing the solvatochromic shift is qualitative correlation of the difference between the ground state and the exited state dipole moments.[18] For dyes **1–23**, the relationship between ΔE_{max} (the transition energy shift between cyclohexane and acetonitrile) and $\Delta\mu$ (the difference between the dipole moment of the ground state and the excited state) is shown in Figure 9 (CI size 14 × 14). Figure 9 shows a weak correlation between the observed ΔE_{max} and the calculated $\Delta\mu$, except for three dye molecules (**16**, **21**, and **23**). Dye **16** has a large substituent around the azomethine bridge, and the optimized dihedral angle is the largest (~60°) among all the dyes; these steric factors make the structure special. In dyes **21** and **23**, the terminal amino group is changed from NEt_2 to $NEt(CH_2CH_2CN)$. Therefore, the solvent effect for **21** and **23** in acetonitrile may be different from that for the other dyes. This relationship between ΔE_{max} and $\Delta\mu$ remains unchanged when the CI size is increased.

(v) Correlation Equations for the Observed and Calculated Spectra. For the main absorption band (both λ_{max} and absorption intensity) and the subabsorption band (λ_{max}), a linear relationship clearly exists. Therefore, the least-squares method was used to obtain the correlation equations for these three properties.

The correlation equations for λ_{max} of the main band are

$$\text{(CI: } 14 \times 14) \ \lambda_{max} \text{ (obsd)} = 1.77\lambda_{max} \text{ (calcd)} - 273 \text{ (nm)} \quad (1)$$

(correlation coefficient 0.88)

$$\text{(CI: } \sim 1260 \text{ config)} \ \lambda_{max} \text{ (obsd)} = 1.76\lambda_{max} \text{ (calcd)} - 284 \text{ (nm)} \quad (2)$$

(correlation coefficient 0.91)

With these equations, the absorption wavelength of the main band can be predicted well.

The correlation equations for the observed molar extinction coefficient and the calculated oscillator strength for the main band are

$$\text{(CI: } 14 \times 14) \ \epsilon \ (\times 10^{-4}) \text{ (obsd)} = 11.4f \text{ (calcd)} - 2.13 \quad (3)$$

(correlation coefficient 0.69)

$$\text{(CI: } \sim 1260 \text{ config)} \ \epsilon \ (\times 10^{-4}) \text{ (obsd)} = 11.7f \text{ (calcd)} - 2.04 \quad (4)$$

(correlation coefficient 0.71)

where ϵ is the molar extinction coefficient and f is the oscillator strength. On the basis of these results, the absorption intensity of the main band can be estimated, and the results are useful for predicting the absorption spectrum of a dye before it is synthesized.

The correlation equations for λ_{max} of the subband are

$$\text{(CI: } 14 \times 14) \ \lambda_{max} \text{ (obsd)} = 1.05\lambda_{max} \text{ (calcd)} - 0.54 \text{ (nm)} \quad (5)$$

(correlation coefficient 0.81)

$$\text{(CI: } \sim 1260 \text{ config)} \ \lambda_{max} \text{ (obsd)} = 1.04\lambda_{max} \text{ (calcd)} - 5.63 \text{ (nm)} \quad (6)$$

(correlation coefficient 0.84)

The prediction of the subabsorption band wavelength improves when the large CI calculation results are used.

Conclusion

The relationships between the observed and the calculated absorption spectra of indoaniline dyes **1–23** were determined. For the main absorption band, the correlation of the absorption wavelength is good, and the correlation is fair for the absorption intensity. For the subabsorption band, the correlation of the absorption wavelength is fair. However, there is no correlation between the observed and the calculated absorption intensity. When the CI

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size is increased, the calculated absorption spectra are improved with respect to the absorption wavelength, especially for the subabsorption band. A qualitative correlation between the solvatochromic shift and the difference between the ground and excited state dipole moments are also obtained.

The possibility of predicting the absorption spectrum of indoaniline dye using the INDO/S calculation with the AM1-optimized geometry has been demonstrated on the basis of these results.

Experimental Section

Spectroscopic Measurements. The dyes were dissolved in Junsei Chemical Co. Ltd. spectrum grade solvents to give 2 × 10^{-5} M solutions, which were read in 1-cm cells with a Hitachi Automatic Recording Spectrophotometer (U-3400).

Preparation and Identification of Dyes. Dyes **1–23** were prepared by oxidative condensation of suitable *p*-phenylenediamines and phenols using ammonium persufate as the oxidant according to the procedure of Vittum and Brown.[4a] All dyes were purified by column chromatography and gave one spot on a thin-layer chromatographic plate.

Dye identification was carried out by the usual method. Melting points were uncorrected.

2-(Acetylamino)-4-[[4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (1): mp 127–128 °C; mass spectrum, *m/e* 311 (M^+), 296 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49. Found: C, 69.23; H, 6.95; N, 13.46.

4-[[4-(Diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (2): mp 107–108 °C; mass spectrum, *m/e* 254 (M^+), 239 ($M^+ - CH_3$). Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.34; H, 7.21; N, 11.01.

4-[[2-Methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (3): mp 84–85 °C; mass spectrum, *m/e* 268 (M^+), 253 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.04; H, 7.74; N, 10.50.

2-Methyl-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (4): mp 101–102 °C; mass spectrum, *m/e* 282 (M^+), 267 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.64; H, 8.13; N, 9.89.

3-Methyl-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (5): mp 104–105 °C; mass spectrum, *m/e* 282 (M^+), 267 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.82; H, 8.11; N, 10.04.

2-Methoxy-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (6): mp 85–86 °C; mass spectrum, *m/e* 298 (M^+), 283 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.24; H, 7.33; N, 9.31.

3-Methoxy-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (7): mp 112–113 °C; mass spectrum, *m/e* 298 (M^+), 283 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.22; H, 7.24; N, 9.37.

2-Fluoro-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (8): mp 128–129 °C; mass spectrum, *m/e* 286 (M^+), 271 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OF$: C, 71.31; H, 6.69; N, 9.78. Found: C, 71.13; H, 6.63; N, 9.80.

3-Fluoro-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (9): mp 127–128 °C; mass spectrum, *m/e* 286 (M^+), 271 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OF$: C, 71.31; H, 6.69; N, 9.78. Found: C, 71.14; H, 6.65; N, 9.79.

2-Chloro-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (10): mp 133–134 °C; mass spectrum, *m/e* 302 (M^+), 287 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OCl$: C, 67.43; H, 6.32; N, 9.25. Found: C, 67.23; H, 6.29; N, 9.23.

3-Chloro-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (11): mp 135–136 °C; mass spectrum, *m/e* 304 (M^+), 289 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OCl$: C, 67.43; H, 6.32; N, 9.25. Found: C, 67.23; H, 6.20; N, 9.22.

2-Bromo-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (12): mp 120–121 °C; mass spectrum, *m/e* 348 (M^+), 333 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OBr$: C, 58.80; H, 5.51; N, 8.07. Found: C, 59.03; H, 5.73; N, 8.25.

3-Bromo-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (13): mp 112–113 °C; mass spectrum, *m/e* 350 (M^+), 335 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{19}N_2OBr$: C, 58.80; H, 5.51; N, 8.07. Found: C, 58.63; H, 5.38; N, 8.27.

2,6-Dichloro-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (14): mp 143–144 °C; mass spectrum, *m/e* 336 (M^+), 321 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{18}N_2OCl_2$: C, 60.54; H, 5.38; N, 8.31. Found: C, 60.36; H, 5.49; N, 8.19.

2-(Acetylamino)-4-[[2-methyl-4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (15): mp 229–230 °C; mass spectrum, *m/e* 325 (M^+), 310 ($M^+ - CH_3$). Anal. Calcd for $C_{19}H_{23}N_3O_2$: C, 70.13; H, 7.12; N, 12.91. Found: C, 70.05; H, 7.33; N, 13.00.

2-(Acetylamino)-4-[[2,6-dimethyl-4-(diethylamino)-phenyl]imino]-2,5-cyclohexadien-1-one (16): mp 149–150 °C; mass spectrum, *m/e* 339 (M^+), 324 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42; N, 12.38. Found: C, 70.51; H, 7.25; N, 12.18.

2-(Acetylamino)-4-[[2-(acetylamino)-4-(diethylamino)-phenyl]imino]-2,5-cyclohexadien-1-one (17): mp 184–185 °C; mass spectrum, *m/e* 368 (M^+), 353 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{24}N_4O_3$: C, 65.20; H, 6.57; N, 15.21. Found: C, 64.96; H, 6.50; N, 14.91.

2-(Acetylamino)-4-[[2-methyl-4-(diethylamino)phenyl]imino]-5-methyl-2,5-cyclohexadien-1-one (18): mp 143–144 °C; mass spectrum, *m/e* 339 (M^+), 324 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42; N, 12.38. Found: C, 70.50; H, 7.34; N, 12.14.

2-[(Trifluoroacetyl)amino]-4-[[2-methyl-4-(diethylamino)phenyl]imino]-5-methyl-2,5-cyclohexadien-1-one (19): mp 127–128 °C; mass spectrum, *m/e* 393 (M^+), 378 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{22}N_3O_2F_3$: C, 61.06; H, 5.64; N, 10.68. Found: C, 60.97; H, 5.61; N, 10.44.

2-(Acetylamino)-4-[[2-methyl-4-(diethylamino)phenyl]imino]-5-chloro-2,5-cyclohexadien-1-one (20): mp 162–163 °C; mass spectrum, *m/e* 359 (M^+), 344 ($M^+ - CH_3$). Anal. Calcd for $C_{19}H_{22}N_3O_2Cl$: C, 63.42; H, 6.16; N, 11.68. Found: C, 63.22; H, 6.16; N, 11.51.

2-(Acetylamino)-4-[[2-methyl-4-[*N*-(2-cyanoethyl)-*N*-ethylamino]phenyl]imino]-2,5-cyclohexadien-1-one (21): mp 147–148 °C; mass spectrum, *m/e* 350 (M^+), 335 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{22}N_4O_2$: C, 68.55; H, 6.33; N, 15.99. Found: C, 68.33; H, 6.40; N, 15.79.

2-(Acetylamino)-4-[[2-methyl-4-[*N*-(2-chloroethyl)-*N*-ethylamino]phenyl]imino]-2,5-cyclohexadien-1-one (22): mp 124–125 °C; mass spectrum, *m/e* 359 (M^+), 344 ($M^+ - CH_3$). Anal. Calcd for $C_{19}H_{22}N_3O_2Cl$: C, 63.42; H, 6.16; N, 11.68. Found: C, 63.20; H, 6.27; N, 11.51.

2-(Acetylamino)-4-[[2-methyl-4-[*N*-(2-cyanoethyl)-*N*-ethylamino]phenyl]imino]-5-chloro-2,5-cyclohexadien-1-one (23): mp 145–146 °C; mass spectrum, *m/e* 384 (M^+), 369 ($M^+ - CH_3$). Anal. Calcd for $C_{20}H_{21}N_4O_2Cl$: C, 62.42; H, 5.50; N, 14.56. Found: C, 62.24; H, 5.54; N, 14.44.

Calculations. Calculations were performed by the INDO/S method (modified for spectral calculations).[15] The electronic repulsion integral was evaluated by the Nishimoto–Mataga formula.[24] All SCF calculations were executed at the closed-shell Hartree–Fock level (RHF). CI calculations included single excited configurations from the ground state and consisted of 14 (occupied) × 14 (vacant) configurations. For several cases, a large CI (near 1260 configurations) calculation considering all vacant orbitals was performed.

The molecular structures of indoaniline dyes **1–23** for the absorption spectrum calculations were determined by the AM1 method[17] without any constraints on the geometrical parameters. Among various possible geometrical isomers, the most stable structure was chosen for the spectrum calculation.

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