any conclusion except the one that some previous objections to resonance are unfounded. Thus we insist that the argument not be based on arbitrary assignments of atomic charges but rather on the more reliable energies and geometries. Among the meaningful questions to be answered are: If there *is* resonance in allyl anion, why is the barrier to C–C rotation so much lower than that in allyl cation? If there *is* resonance in amides, why is the C–O bond not lengthened, relative to a twisted amide? If there is *no* resonance in amides, why is there so large a barrier to rotation about the C–N bond?

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Experimental and Theoretical Study of Near-Infrared Absorbing Naphthoquinone Methide Dyes with a Nonplanar Geometry

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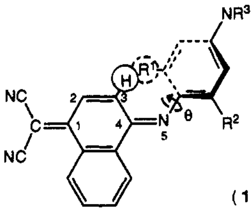
Abstract: The bathochromic shift of the near-infrared absorption spectra of naphthoquinone methide dyes has been observed as a function of increased steric hindrance between the quinone imine and aniline segments. This novel shift that results from the loss of planarity has been examined by means of semiempirical INDO/S and AM1 models. Based on the configuration interaction (CI) analysis, the observed transitions in both the near-infrared and UV regions have been assigned. The introduction of an acetylamino group at the 2-position of aniline ring has caused a bathochromic shift with a remarkable increase in molecular extinction coefficient. In order to interpret these results, both an electronic factor and a steric effect have been analyzed. This interesting color–structure relationship of a nonplanar chromophoric system has been elucidated.

I. Introduction

Conventionally, color chemistry has been primarily concerned with the study of organic compounds which absorb ultraviolet and/or visible light, and thousands of colored molecules have so far been identified. In recent years, there has been a demand for dyes with specific and optimized properties, particularly with respect to a near-infrared absorption (beyond ca. 700 nm). Near-infrared absorbing dyes ("deep-colored" compounds) have attracted considerable attention because of various new applications including diode-laser optical storage media,[1] photosemiconductor layers in laser printers,[2] laser filters,[3] and photochemotherapeutic agents.[4] Despite extensive efforts to prepare highly conjugated compounds suitable for these applications, dyes with such light absorption properties are still rather rare. We have previously reported the syntheses of new deep-colored naphthoquinone methide dyes, 4-(4-dialkylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (**1**), by condensing 1-naphthylmalononitrile[5] with 4-dialkylaminoaniline in the presence of an oxidizing agent under alkaline conditions.[6] These compounds, which are far less conjugated than has traditionally been considered necessary for the attainment of the bathochromic shift, in fact, absorb near-infrared light at 722–761 nm (ϵ_{max} 24 200 – 30 800 dm^3 mol^{-1} cm^{-1}) in $CHCl_3$. These compounds also have good film properties for use as diode-laser optical storage media.

Fundamental studies of this unusual chromophoric system might therefore be useful in elucidating the basic structural features that contribute to a large bathochromic shift. The longest wavelength absorption (band I) for this dye is mainly considered to result from an intramolecular charge transfer corresponding to a migration of an electron from the aniline ring to the quinone imine segment which includes the dicyanomethylene group. As shown in Scheme I, however, the coplanarity between the two segments is disturbed by an intramolecular overcrowding of the molecule. In fact, X-ray analysis of acetylamino derivative (**1d**)[7] indicated that the plane formed by the $C_2{=}C_3{-}C_4{=}N_5$ portion of the quinone imine segment is tilted out of the aniline segment by 42.60°. It is a remarkable feature of these dyes that they can absorb near-infrared light despite such large steric strain. Moreover, the introduction of an acetylamino group at the 2-position in the aniline ring (compound **1d**) results in hydrogen bond formation with the nitrogen atom at the 5-position. The hydrogen bonding enables a bathochromic shift with a large increase in the molecular extinction coefficient compared to the dye (**1a**) (see Table I). The near-

Scheme I



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infrared absorbing properties of dyes such as **1d** are unexpected on the basis of current theories for color–structure relationships in conjugated systems, as discussed below.

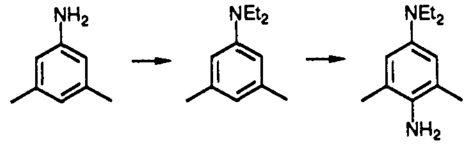
The relationship between color and structure of dyes in terms of molecular orbital theory has been recently reviewed.[8] Generally, the color is attributed to the presence of large conjugated "chromophore" systems.[9] For example, the largest wavelength absorptions of polymethine dyes are bathochromically shifted with increasing chain length.[10] The majority of colored organic compounds are based on a donor–acceptor chromogen, the characteristic feature of which is that the donor group is linked to the acceptor group by an unsaturated bridge. The longest wavelength absorption band is mainly dependent on the excitation from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO), which gives rise to the lowest π–π^* transition. The electronic effects in HOMO – LUMO gaps of dye molecules have been well-studied.[11] The guiding principle for obtaining deep-colored dyes has traditionally involved the introduction of a more powerful donor and acceptor group in each segment of the chromophoric system. Griffiths et al. utilized such structural modification for preparing near-infrared absorbing methine dyes based on indane-1,3-dione.[12] On the other hand, steric crowding in colored systems often has a pronounced effect on the absorption bands. For example, the introduction of the julolidine ring system into several dyes causes a bathochromic shift of the longest wavelength absorption band compared to other dialkylamino group.[13] However, the effects of steric hindrance on the absorption band have been explained only by qualitative arguments,[8b] and have not as yet been established in detail. Consequently, the elucidation of the color–structure relationship for a chromophoric system of the near-infrared dyes with a nonplanar geometry might prove particularly profitable.

Many studies have been undertaken to establish color–structure property relationships on the basis of MO calculations utilizing the PPP–MO method.[8] This method is known to be very reliable for the calculation of the π-electron excitation energies. This method is basically used for π-electron frameworks of planar geometry and is therefore not suitable for a compound with a nonplanar geometry. Actually, in color and constitution of near-infrared absorbing methine dyes,[12] the nonplanar derivatives could not be handled satisfactorily by the PPP–MO method. Hence, a more powerful method is required. Furthermore, an extensive consideration of low-lying excitations is necessary to assign an optical absorption spectrum over a wide-wavelength region. Alternatively, we have attempted to calculate a color-determining transition by using Zerner's all-valence electron INDO/S method.[14] This method takes into account electrons, lone pairs, and π-electrons; thus a higher accuracy relative to the PPP–MO method is expected. In addition, an intramolecular hydrogen bond of the dye has been described qualitatively by AM1 method.[15] In the present paper, we extend this work in three related directions. First, we have examined the relationship between the structure and the longest wavelength absorption band of the near-infrared absorbing dyes with a nonplanar geometry. Second, we have assigned the short-wavelength absorption band observed in UV region. The influence of the steric effects on the absorption properties in the UV region is also discussed. Finally, the specific effect of an acetylamino group at the 2-position in the aniline ring on absorption band has been analyzed on the basis of both electronic factors and steric effects.

II. Experimental and Computational Details

Melting points are uncorrected. Absorption spectra were measured using a JASCO Ubest-30 UV/Vis spectrophotometer. ^{1}H NMR spectra were taken on a Hitachi R-90H spectrometer. IR spectra were obtained by using a JASCO FT/IR 5000 spectrometer on KBr pellets. Mass spectra were taken on a Hitachi M-80A spectrometer, and elemental analyses were obtained using a Perkin-Elmer 240C C,H,N analyzer. The syntheses of dyes **1a**,[6] **1b**,[6] and **1d**[7] (see Table I) were reported previously.

Materials. 1-Naphthylmalononitrile was synthesized by a previously described method.[5] 4-Diethylamino-2,6-dimethylaniline was synthesized from 3,5-xylidine as follows.



N,N-Diethyl-3,5-xylidene. C_2H_5I (91 mmol) was added to a mixture of 3,5-xylidene (41 mmol), *N*-methyl-2-pyrrolidone (63 mmol), and Na_2CO_3 (91 mmol). The reaction mixture was stirred for 24 h under reflux conditions, poured into water, and extracted with Et_2O. Removal of Et_2O and distillation of the residue under vacuum gave *N,N*-diethyl-3,5-xylidine in 88% yield: mp 50–51 °C; ^{1}H NMR ($CDCl_3$, TMS) 1.14 (t, 6 H), 2.25 (s, 6 H), 3.31 (q, 4 H), 6.31 (s, 3 H).

4-Diethylamino-2,6-dimethylaniline. *N,N*-Diethyl-3,5-xylidene (29.4 mmol) was dissolved in concd HCl (7.3 mL) – water (15.6 mL) solution. To the solution at 0 °C, $NaNO_2$ (32.3 mmol) was added slowly; the mixture was stirred for 1 h. After the addition of concd HCl (18.75 mL) and water (20.6 mL) to the reaction mixture, Zn powder (129 mmol) was added in small portions to the solution; the mixture was stirred for 1 h, during which time the reaction solution turned colorless. The solution was then filtered in order to remove unreacted zinc, made basic with NaOH, and extracted with Et_2O. After Et_2O was removed, the residue was distilled under vacuum to give a heavy yellow oil, 4-diethylamino-2,6-dimethylaniline, in 49% yield: bp 130 °C (2 mmHg); ^{1}H NMR ($CDCl_3$, TMS) 1.07 (t, 6 H), 2.16 (s, 6 H), 3.1 (br, 2 H), 3.18 (q, 4 H), 6.47 (s, 2 H).

Preparation of 4-(4-Diethylamino-2,6-dimethylphenylimino)-1,4-dihydronaphthylidenemalononitrile (1c). To an acetone–concd NH_3 aqueous solution of 1-naphthylmalononitrile (1.31 mmol) and 4-diethylamino-2,6-dimethylaniline (2.61 mmol) at room temperature, an aqueous solution of $(NH_4)_2S_2O_8$ (6.56 mmol) was added slowly. After the mixture was stirred for 30 min at room temperature, the acetone solvent was removed. The product was filtered off, washed with water, dried, and chromatographed on silica gel (Wakogel C-300) using CH_2Cl_2 as an eluent. Dye **1c** was obtained in 25% yield and recrystallized from ethanol: mp 147–148 °C; λ_{max} (C_6H_6) 791 nm (ϵ_{max} 7700 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR ($CDCl_3$, TMS) 1.20 (t, 6 H, $2CH_3$), 2.02 (s, 6 H, Ar CH_3), 3.38 (q, 4 H, $2CH_2$), 6.47 (s, 2 H, Ar H), 6.72 (d, 1 H, J = 10.2 Hz, quinoid H), 7.44 (d, 1 H, J = 10.2 Hz, quinoid H), 7.54–7.86 (m, 2 H, Ar H), 8.79–8.90 (m, 2 H, Ar H); IR (KBr) 2218 cm^{-1} ($C\equiv N$); mass spectrum, m/e 380 (M^+), 365 ($M^+ - CH_3$). Anal. Calcd for $C_{25}H_{24}N_4$: C, 78.92; H, 6.36; N, 14.72. Found: C, 78.81; H, 6.38; N, 14.52.

Computational Details. The absorption wavelength and oscillator strength were calculated theoretically by the semiempirical MO INDO/S method. The INDO/S calculation was modified in order to reproduce the spectroscopic properties from an INDO/1 scheme.[14] The two-center electron repulsion integrals were evaluated by the Mataga–Nishimoto formula.[16] We performed the configuration interaction (CI) calculation up to 196 configuration functions by adapting the occupied orbitals of (HOMO–13 to HOMO) and the vacant orbitals of (LUMO to LUMO+13). Each configuration function was generated through the single excitation (S-CI) from the ground-state function.

The geometries used in this calculation were chosen from the structure established by X-ray diffraction data of dye **1d**.[7] For the other geometries we simply replaced $NHCOCH_3$ by H or CH_3, adopting standard bond lengths and bond angles.[17] Optimizations of the dihedral angle between

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Table 1. The Observed and Calculated Longest Wavelength Absorption Band for Dyes **1**

dye[a]	R^1	R^2	λ_{max}/nm (ϵ_{max}) (C_6H_6)	$\Delta\lambda$[b]	dihedral angle (θ),[c] deg	INDO/S λ_{max}	f[d]
1a	H	H	711 (25 200)		47.5	546.3	0.7547
1b	H	Me	731 (27 100)	20	47.5	555.9	0.7467
1c	Me	Me	791 (7 700)	80	63.1	580.3	0.4178
1d	H	NHAc	756 (51 200)	45	40.7[e]	569.5	0.9117

[a] $R^3 = R^4 =$ Et. [b] $\Delta\lambda_{max} = \lambda_{max}$ (**1b–d**) − λ_{max} (**1a**). [c] Dihedral angle between quinone imine moiety ($C_2{=}C_3{-}C_4{=}N_5$) and aniline ring was optimized by the AM1 method. [d] Oscillator strength. [e] An X-ray study of **1d** produced a dihedral angle of 42.6°.

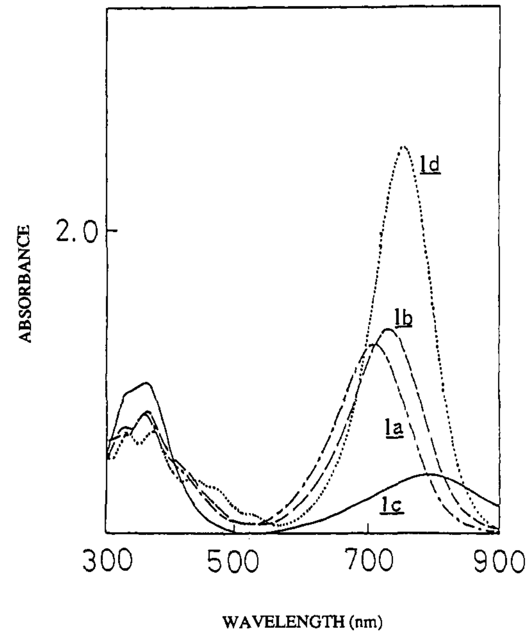

Figure 1. Absorption properties of naphthoquinone methide dyes (**1**) (5.0×10^{-5} M) in C_6H_6 solution: **1a** —·—·—; **1b**, — — —; **1c**, ——; **1d**, - - -.

quinone imine and aniline segments were performed by the AM1 method, during which other degrees of freedom of the geometry were fixed to the experimental X-ray value.

III. Results and Discussion

A. The Longest Wavelength Absorption Band and Structures. The observed and INDO/S calculated longest wavelength absorption band (band I) for dyes **1** in near-infrared region are given in Table I. The dihedral angle between the quinone imine and the aniline segments have been optimized by using the AM1 method where θ is the twist angle of the aniline ring in a counterclockwise direction as shown in Scheme I. The optimization resulted in values of θ of 47.5° for both **1a** and **1b**, whose absorptions are 711 nm and 731 nm in benzene, respectively. To obtain further insight into the steric effect on the absorption spectra, we synthesized 4-(4-diethylamino-2,6-dimethylphenylimino)-1,4-dihydronaphthylidenemalononitrile (**1c**) by condensing 1-naphthylmalononitrile with 4-diethylamino-2,6-dimethylaniline in the presence of $(NH_4)_2S_2O_8$ under alkaline conditions. Dye **1c** absorbs near-infrared light at 791 nm in benzene, whose wavelength is longer than that of the corresponding naphthoquinone methide dye (**1a**) by 80 nm (see Table I). The spectral features of these dyes are shown in Figure 1, indicating that the molecular extinction coefficients of band I for dyes **1** are significantly influenced by substituents at 2,6-positions in the aniline ring. These results suggested that band I was dependent on the steric hindrance between the quinone imine (acceptor) and the aniline (donor) segments. Interestingly, the large bathochromic shift was observed with large steric hindrance by the introduction of 2,6-dimethyl groups into the aniline ring. The optimization of the dihedral angle of dye **1c** produced a value of 63.1° by the AM1 method, and the INDO/S calculation using this value suggested a bathochromic shift of the absorption spectra (Table I). Hence, we examined the relationship between the λ_{max} and dihedral angle. In Figure 2, the λ_{max} value and oscillator strength calculated by the INDO/S method are plotted against the dihedral angle for dye **1a**. The decrease in oscillator strength can be explained by a poor overlap of wave functions between the donor and acceptor segments along with the decrease of the coplanarity. However, the calculated results indicated that the λ_{max} value

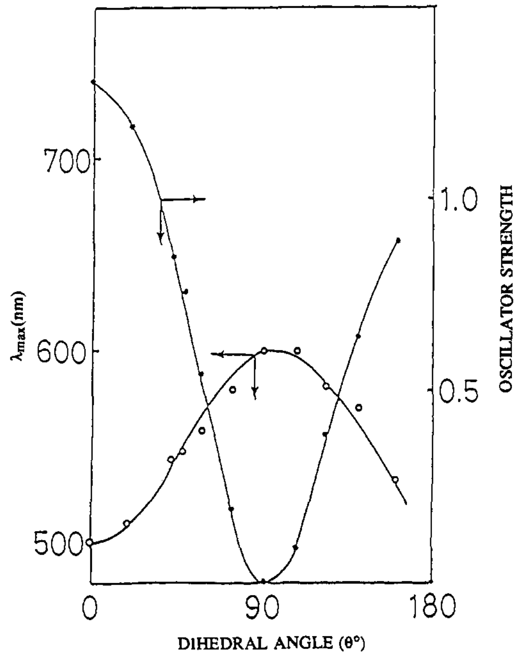

Figure 2. Plots of the longest wavelength absorption band and oscillator strength (f) against dihedral angle (θ) for dye **1a**.

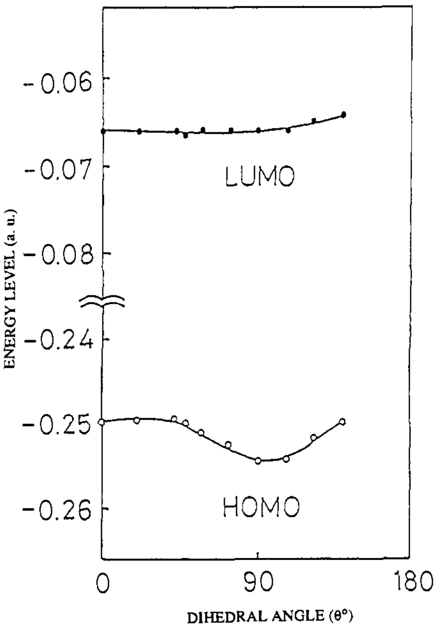

Figure 3. HOMO and LUMO energy levels against dihedral angle (θ) for dye **1a**.

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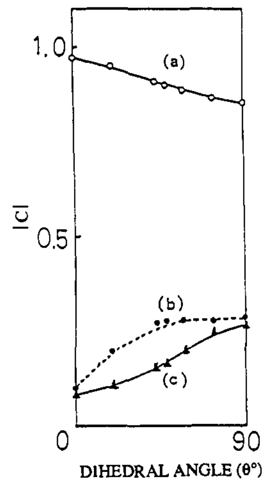

Figure 4. The absolute value of the CI coefficient of the main transition for the long-wavelength absorption maxima plotted against dihedral angle (θ): (a) HOMO → LUMO, (b) (61)th orbital → LUMO, (c) HOMO → next LUMO.

Table II. Comparison between Observed and Calculated Absorption Spectra of Dye **1a**; the Dihedral Angle between Quinone Imine and Aniline Segments Is 47.5°

band	λ_{max}/nm obsd (ϵ_{max})[a]	λ_{max}/nm calcd (f^b)	calculated assignment
I	711 (25 200)	546.3 (0.7547)	HOMO → LUMO (80.9%)[c] (61)th orbital → LUMO (7.5%) HOMO → NLUMO[d] (2.8%)
II	361 (15 900)	362.9 (0.6974)	(61)th orbital → LUMO (30.8%) NHOMO[e] → LUMO (19.5%) HOMO → LUMO (12.8%)
III	321 (13 100)	335.7 (0.2503) 321.3 (0.0360) 313.7 (0.0149) 309.1 (0.3982)	

[a] In C_6H_6. [b] Oscillator strength. [c] (CI coefficient)^2 × 100%. [d] Next LUMO. [e] Next HOMO, the schematic drawing of which is shown in Figure 5.

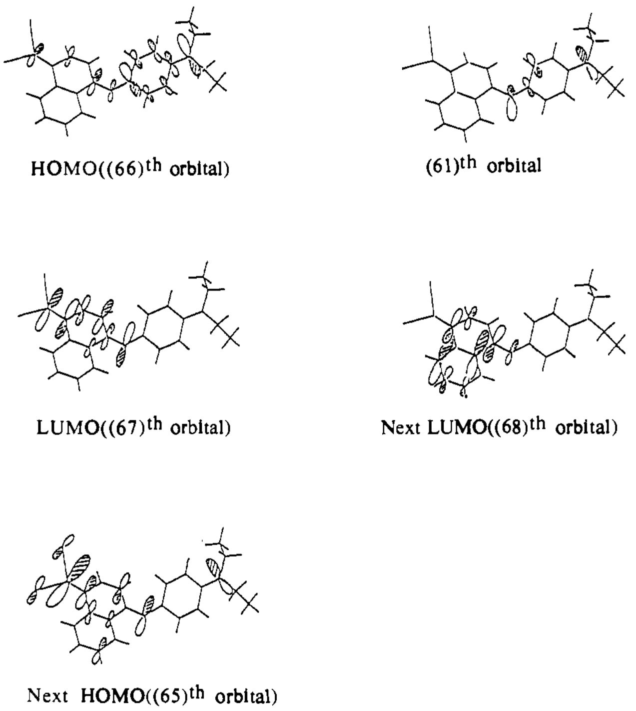

Figure 5. A schematic drawing of important orbitals related to the transitions for the absorption bands I and II for dye **1a**; the dihedral angle between the quinone imine and aniline segments is 47.5°.

Table III. Observed and Calculated Second Absorption Bands for Dyes **1**

dye[a]	R^1	R^2	dihedral angle (θ),[b]	band II obsd (ϵ_{max})	band II calcd (f^c)
1a	H	H	47.5	361 (15 900)	362.9 (0.6974)
1b	H	Me	47.5	363 (16 400)	365.1 (0.6872)
1c	Me	Me	63.1	363 (20 000)	359.7 (1.0065)
1d	H	NHAc	40.7[d]	372 (13 700)	365.7 (0.5268)

[a] $R^3 = R^4 =$ Et. [b] Optimized by AM1 method. [c] Oscillator strength. [d] An X-ray study of **1d** produced a dihedral angle of 42.6°.

shifted to longer wavelength with an increase in dihedral angle. Surprisingly at θ = 90°, the longest λ_{max} value (608 nm) was obtained. These results could not be explained on the basis of an energy gap between HOMO and LUMO, because the energy gap was increased along with the increase of dihedral angle as shown in Figure 3. The results contrast with the recent work of Detty et al.,[11b] where AM1-determined HOMO – LUMO gaps for model pyrylium dyes give a good correlation with the modification of their dihedral angles due to the steric repulsion. Therefore, the specific steric effect must be explained based on configuration interaction (CI) calculations.[18] Actually, the CI calculations have reproduced a bathochromic shift with an increase in the dihedral angle. Figure 4 shows the CI coefficient of the main transition for the longest wavelength absorption band (band I) against dihedral angle. The HOMO → LUMO excitation character decreased with an increase in the dihedral angle in the CI stage, while the contribution of the (61)th orbital[19] → LUMO and HOMO → NLUMO (next LUMO) excitations increased. The inclusion of these transitions might cause a decrease in the transition energy for band I, and, consequently, a bathochromic shift of λ_{max} would be produced. The schematic drawing of important orbitals related to the transition for band I are shown in Figure 5. Thus the experimental results were explained on the basis of CI calculations.

B. Assignment of the Transition. Based on the CI calculation, the observed transitions for dye **1a** were assigned where the dihedral angle between the quinone imine and aniline segments was optimized by the AM1 method (47.5°). The results are summarized in Table II. The main bands in the absorption spectra shown in Figure 1 were reproduced by our calculations, except the weakest bands (λ_{obsd} 321 nm). As discussed in section A, the observed band I in the near-infrared region was characterized by configuration interaction calculations, mainly as the mixture of configurations HOMO → LUMO, (61)th orbital → LUMO, and HOMO → NLUMO. The transition was deemed to be mainly of a charge-transfer type. For band II (λ_{obsd} 361 nm), the calculated oscillator strength was 0.6974, slightly lower than that for band I. The characteristic feature of band II was the involvement of a NHOMO (next HOMO) → LUMO excitation and was mainly described as a transition inside the quinone imine segment. For the band III, we assign the observed absorption (321 nm) to calculated transitions in this region.

In Table III, the observed and calculated wavelengths of band II are shown for dye **1**. The calculated λ_{max} values of band II were in good agreement with experiment, where the observed molecular extinction coefficient increased along with an increase in the dihedral angle. Our calculated results reproduced this feature and are given in Figure 6. The oscillator strength of the transition for band II was significantly increased by the increase of the dihedral angle, while that of band I decreased. The oscillator strength weakened to near zero for the almost-planar geometry (θ ≃ 0°), while the perpendicular structure (θ ≃ 90°) gave rise

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[18] This result could not be also obtained on the basis of the energy gap between the HOMO and LUMO corresponding to the lowest excited singlet state (S_1)

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

where ΔE is the difference of orbital energies and $J_{HOMO,LUMO}$ and $K_{HOMO,LUMO}$ are the molecular Coulomb and exchange integrals, respectively.

[19] The (61)th orbital of **1a** is the 61st one from the bottom, which has the character of a lone pair of imino nitrogen as shown in Figure 5. The HOMO is orbital number 66 for reference.

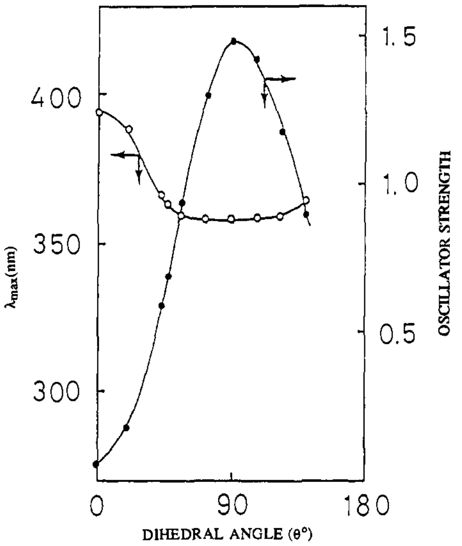


Figure 6. Plots of λ_{max} and oscillator strength (f) of band II against dihedral angle (θ) for dye **1a**.

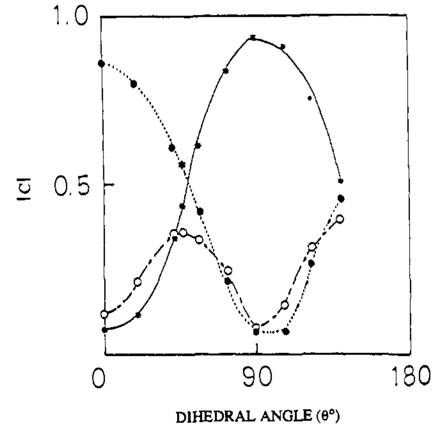
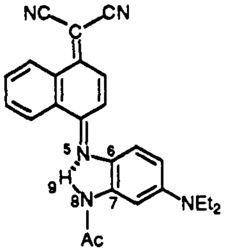


Figure 7. The absolute value of the CI-coefficient of the main transition for band II plotted against dihedral angle (θ): --●--●--, (61)th orbital → LUMO; —*—*—, next HOMO → LUMO; —o—o-, HOMO → LUMO.

to the largest value. In Figure 7, the character of the transition for band II is shown by using CI coefficients. At small dihedral angle, (61)th orbital → LUMO was the major component of the transition corresponding to the charge-transfer character from the aniline segment including the lone pair of the imino nitrogen to the quinone imine segment. In such a transition, the overlap of the excited-state and the ground-state wave functions could not be larger than that of the transitions on one ring. This could explain the small oscillator strength observed. On the other hand, along with the increase of dihedral angle (~90°), the contribution from NHOMO to LUMO increased, which corresponds a transition inside of the quinone imine segment (see Figure 5), thus augmenting the oscillator strength.

C. Absorption Property Changes Specifically Induced by the Introduction of an Acetylamino Group. As shown in Table I, dye **1d** absorbs near-infrared light at 756 nm (ϵ_{max} 51 200 dm^3 mol^{-1} cm^{-1}) in benzene. The introduction of an acetylamino group at the 2-position in the aniline ring produced a 45-nm bathochromic shift, and, in particular, the molecular extinction coefficient was almost twice that of corresponding dye **1a**. These absorption properties are the result of the electronic factor and steric effect of the acetylamino group. An X-ray analysis of dye **1d** has indicated that an intramolecular hydrogen bond is formed between the imino nitrogen and peptide segments in the acetylamino group,[7] which is considered to influence the absorption properties significantly. In order to study the hydrogen bonding effect, the hydrogen bond distance was modified by changing the angle of H_9–N_8–C_7 in our calculations. Table IV shows the effect of the intramolecular hydrogen bond on the dihedral angle, λ_{max}, and the oscillator strength of dye **1d**. The intramolecular hydrogen bond induced a decrease in the dihedral angle. Thus, extended conjugation between the quinone imine and aniline segments explains the increased oscillator strength due to the corresponding enlargement of the overlap integrals. However, the absorption maxima were scarcely influenced, which might imply that a balance exists between the electronic factor and steric effect of the intramolecular hydrogen bond. Furthermore, the X-ray analysis of dye **1d** also indicated that the phenyl ring and acetylamino group are almost coplanar, which suggested efficient conjugation of the aniline (donor) segment. In order to understand this effect on the absorption properties, we have calculated the absorption band of the molecule with $NHCOCH_3$ replaced by $OCOCH_3$ (**1e**). This substitution produces a molecule without an intramolecular hydrogen bond but with a comparable size of conjugation of $NHCOCH_3$. The geometry of **1e** was assumed to be the same as that of **1d**. Table V shows the results, including those for **1a** and **1b**, where the dihedral angle is kept at 42.6° (as determined by X-ray for **1d**). Dyes **1d** and **1e** show larger oscillator strengths than **1a** and **1b**. As $NHCOCH_3$ and $OCOCH_3$ groups have a larger π-conjugation than H and CH_3 groups, the extended conjugation with the aniline ring would increase the oscillator strength. Then, by comparing **1d** and **1e** in Table V, the hydrogen bond in **1d** can be considered to cause a bathochromic shift on the absorption band.

Table IV. Effect of Intramolecular Hydrogen Bond on Dihedral Angle, λ_{max}, and Oscillator Strength of Dye **1d**



1d

H_9–N_8–C_7 angle (θ), deg	N_5–H_9, distance (Å)	dihedral angle (θ),[a] deg	INDO/S	
			λ_{max}	f[b]
100	1.935	39.5	570.0	0.9318
115.75[c]	2.180	40.7	569.5	0.9117
130	2.423	42.3	568.5	0.9021
140	2.595	43.3	569.3	0.8910

[a] Optimized by AM1 method. [b] Oscillator strength. [c] Determined by X-ray analysis.

Table V. Calculated Results for the Absorption Band (INDO/S); Dihedral Angle between the Quinone Imine and Aniline Segments Is 42.6°

dye[a]	R^1	R^2	λ_{max}/nm	f[b]
1d	H	NHAc	571.3	0.892
1e	H	OAc	550.1	0.879
1a	H	H	543.8	0.845
1b	H	Me	553.1	0.836

[a] $R^3 = R^4$ = Et. [b] Oscillator strength.

Our calculated results indicated that the acetylamino group introduced at the 2-position of the aniline ring played a significant role in electronic and steric effects on the absorption properties.

IV. Conclusions

Calculations using the INDO/S method reproduced a bathochromic shift of λ_{max} with an increase in the steric torsion between the quinone imine and the aniline segments for naphthoquinone methide near-infrared dyes. This feature was interpreted in terms of a configuration interaction. Furthermore, the observed transitions found in the UV region were successfully assigned by our INDO/S calculations. The transition inside of the quinone imine segment associated with the spectrum in the UV region was also

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influenced by the steric hindrance between the quinone imine and aniline segments.

The introduction of an acetylamino group at the 2-position in the aniline ring produced a specific effect on the absorption properties, which could be explained on the basis of electronic factors and steric effects: (1) the intramolecular hydrogen bond between the imino nitrogen and the peptide segment in the acetylamino group restores the planarity and strengthens the π-conjugation, overcoming the steric hindrance of the two segments; (2) the enhancement of π-conjugation in the aniline (donor) segment increases the oscillator strength. This work demonstrates that INDO/S and AM1 calculations are of considerable value in elucidating the color–structure relationship for chromophoric systems with nonplanar geometries. The steric hindrance and an intramolecular hydrogen bond between donor and acceptor segments have been found to influence the absorption properties. Thus, the introduction of a suitable substituent, such as an acetylamino group, will cause a bathochromic shift with an increase in molecular extinction coefficient. These results afford a useful insight into the molecular design of new near-infrared dyes.

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Analysis of Solvent Effects on the Menshutkin Reaction

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Abstract: The reaction between ammonia and methyl bromide, which has been taken as a model for the Menshutkin reaction, has been studied through ab initio methods in the gas phase and in solution using discrete and continuum representations of the solvent. The solvent effect on this reaction bears a resemblance with other S_N2 reactions but also exhibits some differences with them. The main results turn out to be, on one hand, a decrease in the energy barrier upon increase in solvent polarity, and, on the other hand, the transition state is found earlier along the reaction coordinate, showing the participation of solvent parameters in the reaction coordinate. The polarization of the solute by the reaction field created by the solvent polarization is one of the most important aspects of the coupling between the solvent and the chemical system. This translates into an increase of the weight of the charge-transfer configuration with respect to the weight in the gas phase. Likewise, fluctuations increasing the reaction field are stabilized by instantaneous changes in the electronic distribution of the solute.

Introduction

One hundred years ago[1,2] Menshutkin published his landmark study about the solvent effect on the alkylation of tertiary amines by alkyl halides. Nowadays, in his honor, this reaction is known by his name. He found that the reaction rate increased dramatically with the polarity of the solvent employed, so he concluded that a reaction cannot be separated from the medium in which it is carried out. Unfortunately, the deep implications of this pioneering study of Menshutkin have not been taken into account for many years.

The Menshutkin reaction is a special kind of S_N2 reaction where the reactants are uncharged, in contrast to the most usual S_N2 reactions where one of the reactants is charged. In the last few years there has been an outgrowing number of theoretical papers dealing with the solvent effect on S_N2 reactions. For instance, the reaction of chloride with methyl chloride has received recently considerable attention.[3-21] From the analyses made so far on this particular reaction, the effects of solvent molecules have been classified into two main classes: static and dynamic.

The static effect of solvent molecules (also known as equilibrium effect) implies a separation between the chemical system and the bath. The solvent is equilibrated for each given geometry of the solute, so it plays a passive role in the chemical process. The bath makes only a different energetic contribution to the free energies of reactants and transition state, thus leading to a change in activation free energy and hence in the reaction rate.

Solvent effects which require a more dynamical treatment of solvent coordinates are called nonequilibrium or dynamic effects. The extent of equilibration of the solvent has been shown to be governed by the strength of the solute–solvent coupling, by the sharpness of the barrier, and by the characteristic time scale for the solute reaction motion. If the characteristic time scale for solvent reorganization is much slower than the time scale for solute reaction motion, nonequilibrium solvation effects on rate constants

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