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# Site-Specific Substituent Effect on the Photoinduced Formation of Benzalaniline Radical Anion in 2-Methyltetrahydrofuran at 77 K

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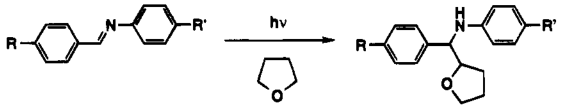
**Abstract:** Photochemical properties of benzalaniline derivatives have been studied by the absorption spectrum of the transient species in 2-methyltetrahydrofuran (MTHF) at 77 K. A photoinduced electron transfer from MTHF to the second photoexcited state of a benzalaniline was suggested on the basis of the observation of the radical anion. In the series, only the derivative with an electron-withdrawing group at the 4′-position efficiently gave the radical anion. The CNDO/S calculation indicated considerable differences in the dipole moment and the positive charge localization between 4- and 4′-substituted derivatives at the second photoexcited state, which induces the site-specific substituent effect.

## Introduction

Benzalaniline is an aromatic Schiff's base which is considered to have an electronic structure similar to that of stilbene.[1] However, the photophysical and photochemical properties of benzalaniline are considerably different from those of stilbene. Benzalaniline is known to have a characteristic structure, and the structural difference is mainly proposed to cause the difference in properties between benzalaniline and stilbene. The *N*-phenyl group ($Ph_N$) is rotated out of the plane of the conjugated system consisting of the *C*-phenyl ($Ph_C$) and imine groups, while $\pi$ conjugation extends over the whole molecule in the case of stilbene.[2] Thus, participation of the nitrogen lone pair in the conjugated system induces rotation of the $Ph_N$ with the twist angle $\theta_N$, resulting in two energetically more favorable individual conjugated systems ($8\pi$, $6\pi + 2n$) than the planar conjugation of the whole molecule ($14\pi$).[3] Furthermore, the split of the conjugated system allows independent "local" electronic transitions such as $\pi-\pi^*$ at $Ph_N$, $\pi-\pi^*$ at $Ph_C$, and $n-\pi^*$ and a charge transfer (CT) state at the anil group. Accordingly, one should consider that the electronic structure is not a simple layer of excited states as in the case of an aromatic olefin but a group of local and CT excited states with different energy levels similar to a metal complex. Conversion between the excited states is, therefore, considerably inefficient compared to that of a normal aromatic olefin. The electronic structure provides unusual properties of the photoexcited states, for example, no mirror-imaged fluorescence and absorption spectra[4] and a considerable solvent shift of the absorption bands.[5] This consideration allows rational interpretation of the electronic absorption bands[2,6,7] and the $^{13}C$ NMR chemical shift of the azomethine carbon.[8] In a previous paper, we proposed that the photoexcited state of benzalaniline shows a site-specific substituent effect on the reactivity.[9] Photoirradiation of benzalanilines in tetrahydrofuran (THF) afforded a 1:1 solvent adduct (eq 1). The 4-MeO (R = MeO, R′ = H) and the 4′-CN (R = H, R′ = CN) derivatives gave the adducts in high yields. On the contrary, the yields of the adducts from the 4′-MeO and 4-CN derivatives were very low. Thus, the substituent which is expected to give the electron flow from $Ph_C$ to $Ph_N$ is effective for the photochemical adduct formation. The key intermediate for a CN derivative was proposed to be the radical anion; however, the mechanism for preferential formation of the 4′-CN radical anion was not clear. In this paper, we report an unusual site-specific substituent effect on the photoinduced formation of the radical anion in a low-temperature matrix in terms of correlation between the photophysical and photochemical properties.



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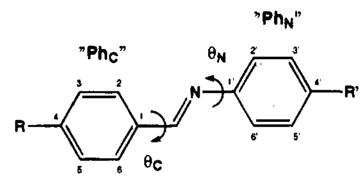

| R | R' |
|---|---|
| H | H |
| MeO | H |
| Me | H |
| Cl | H |
| $CF_3$ | H |
| CN | H |
| H | MeO |
| H | Me |
| H | Cl |
| H | COOEt |
| H | $CF_3$ |
| H | CN |

## Experimental Section

**Materials.** Spectroscopic grade solvents were obtained from Dojin Chemical Co. and purified by distillation over $CaH_2$ prior to use. Benzalaniline was obtained from Tokyo Kasei Co. Other derivatives

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[1] Pratt, A. C. *Chem. Soc. Rev.* **1977**, 64.

[2] Ashraf El-Bayoumi, M.; El-Aasser, M.; Abdel-Halim, F. *J. Am. Chem. Soc.* **1969**, *93*, 586–590.

[3] Ismailski, V. A.; Smirnov, E. A. *J. Gen. Chem. USSR* **1956**, *26*, 3389.

[4] Belletete, M.; Durocher, G. *Can. J. Chem.* **1982**, *60*, 2332.

[5] Belletete, M.; Scheuter-Lamalle, B.; Baril, L.; Durocher, G. *Can. J. Spectrosc.* **1977**, *22*, 31.

[6] Smith, W. F. *Tetrahedron* **1963**, *19*, 445.

[7] Minkin, V. I.; Zhdanov, Y. A.; Medyantzeva, E. A.; Ostroumov, Y. A. *Tetrahedron* **1967**, *23*, 3651.

[8] Kawasaki, A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 223.

[9] Ishida, A.; Sugita, D.; Takamuku, S. *J. Photochem. Photobiol., A* **1992**, *65*, 197.

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were synthesized by condensation of a *para*-substituted benzaldehyde and aniline, or of benzaldehyde and a *para*-substituted aniline, with benzenesulfonic acid as a catalyst. The synthetic procedure is available in the literature.[10] All benzalanilines were purified by column chromatography on alumina with a hexane−ether mixture eluent and successive recrystallization.

**Low-Temperature Matrix Measurements.** A sample solution (5 mmol $dm^{-3}$) was degassed by freeze−pump−thaw cycles under high vacuum and sealed in a 40 × 10 × 1 $mm^3$ Suprasil cell. Photoirradiation was carried out in liquid nitrogen with a rectangular quartz Dewar vessel and a 500-W ultra-high-pressure mercury lamp attached to a focusing mirror system and a water filter. $\gamma$-Ray irradiation was carried out in liquid nitrogen with a $^{60}Co$ source ($3.7 \times 10^{14}$ Bq), and the dose was 700 Gy. The absorption spectrum was measured in liquid nitrogen with a rectangular quartz Dewar vessel and a multichannel spectrometer (Otsuka Electronics MCPD-1000). These experiments were carried out under a rather high concentration of the substrate (5 mmol $dm^{-3}$) compared to the usual matrix isolation experiments. The present determination method for the radical anion needed a sufficient amount of the substrate to retain the linearity.

**Laser Flash Photolysis.** A 1 mmol $dm^{-3}$ THF solution of 4′-cyanobenzalaniline was saturated with Ar by bubbling for 10 min and sealed in a 40 × 10 × 10 $mm^3$ rectangular Suprasil cell. A transient absorption spectrum was measured at room temperature by use of a conventional nanosecond laser flash photolysis system with a Q-switched Nd:YAG laser (Quantel Brilliant) and a fourth harmonic generator (266 nm, 20 mJ, 4 ns).

**Absorption Spectra at Room Temperature.** For determination of a band system, an absorption spectrum of a benzalaniline derivative (100 $\mu$mol $dm^{-3}$) was measured in *n*-pentane or cyclohexane at room temperature with a UV−vis spectrometer (Hitachi 150). For observation of the wavelength shift upon changing the solvent properties, an absorption spectrum of a benzalaniline derivative (100 $\mu$mol $dm^{-3}$) was measured in a series of solvents at room temperature.

**Photochemical Reaction at Room Temperature.** A 5 mmol $dm^{-3}$ THF solution of a benzalaniline derivative was saturated with argon by bubbling for 10 min and sealed in a quartz tube. Photoirradiation was carried out with a 350-W high-pressure mercury lamp and a merry-go-round apparatus at room temperature. The reaction was monitored by GLC (Shimazu GC-7A, OV-17, 1 m) and the product was determined by an internal standard. The GLC peak of a 1:1 adduct was identified by GC−MS analysis. The 1:1 THF adduct of a CN derivative was isolated as a mixture of diastereomers by column chromatography on alumina with a hexane−ether mixture eluent and analyzed by MS (JEOL DX-300), $^{13}C$ NMR (JEOL JNM-GSX 270), and elemental analysis (Perkin-Elmer 240C).

***N*-[(Tetrahydro-2-furanyl)(4-cyanophenyl)methyl]aniline**: colorless crystal from ethanol; mp (uncorrected) 114−116 °C; MS *m/z* (rel intens) 278 ($M^+$, 7), 207 ($M^+ - C_4H_7O$, 100), 104 (3), 77 (8), 71 (9); $^1H$ NMR (270 MHz, $CDCl_3$) (diastereomer no. 1) $\delta$ 1.60−1.98 (m, 4H), 3.76−3.95 (m, 2H), 4.18−4.25 (m, 1H), 4.45 (d, $J$ = 4.3 Hz, 1H), 4.57 (br s, 1H), 6.46 (d, $J$ = 7.6 Hz, 2H), 6.62−6.68 (m, 1H), 7.03−7.10 (m, 2H), 7.48-7.61 (m, 4H); (diastereomer no. 2) $\delta$ 1.60−1.98 (m, 4H), 3.76−3.95 (m, 2H), 3.97−4.06 (m, 1H), 4.33 (d, $J$ = 5.3 Hz, 1H), 4.74 (br s, 1H), 6.46 (d, $J$ = 7.6 Hz, 2H), 6.62−6.68 (m, 1H), 7.03−7.10 (m, 2H), 7.48-7.61 (m, 4H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) (diastereomer no. 1) $\delta$ 25.46 ($CH_2$), 27.60 ($CH_2$), 60.75 (CHNH), 68.77 ($CH_2O$), 81.45 (CHO), 111.12 (Ar, *C*CN), 113.64 (Ar, CH), 118.84 (CN), 127.98 (Ar, CH), 128.62 (Ar, CH), 129.11 (Ar, CH), 132.09 (Ar, CH), 146.11 (Ar, *C*CHNH), 147.60 (Ar, CNH); (diastereomer no. 2) $\delta$ 25.70 ($CH_2$), 28.72 ($CH_2$), 61.27 (CHNH), 68.77 ($CH_2O$), 82.35 (CHO), 111.12 (Ar, *C*CN), 113.71 (Ar, CH), 118.00 (CN), 127.98 (Ar, CH), 128.62 (Ar, CH), 129.11 (Ar, CH), 132.43 (Ar, CH), 146.56 (Ar, *C*CHNH), 147.95 (Ar, CNH). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.65; H, 6.27; N, 9.89.

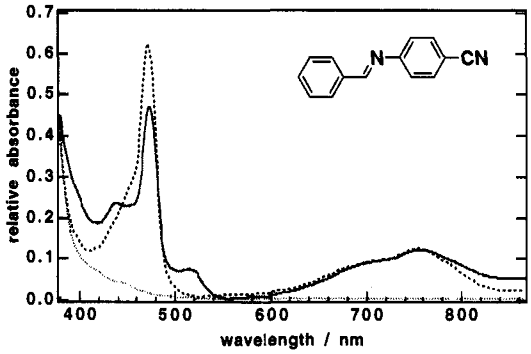

**Figure 1.** Absorption spectra of 5 mmol $dm^{-3}$ 4′-cyanobenzalaniline in MTHF at 77 K before irradiation (dotted line), after 10 min of photoirradiation (solid line), and after 5 min of $\gamma$-ray irradiation (dashed line).

***N*-[Phenyl(tetrahydro-2-furanyl)methyl]-4-cyanoaniline**: colorless crystal from ethanol; mp (uncorrected) 100−102 °C; MS *m/z* (rel intens) 278 ($M^+$, 7), 207 ($M^+ - C_4H_7O$, 100), 129 (12), 102 (9), 91 (2), 71 (5); $^1H$ NMR (270 MHz, $CDCl_3$) (diastereomer no. 1) $\delta$ 1.69−1.97 (m, 4H), 3.71−3.84 (m, 2H), 3.98−4.07 (m, 1H), 4.41−4.45 (m, 1H), 5.18 (br s, 1H), 6.49 (d, $J$ = 8.6 Hz, 2H), 7.27−7.35 (m, 7H); (diastereomer no. 2) $\delta$ 1.69−1.97 (m, 4H), 3.71−3.84 (m, 2H), 3.90−3.95 (m, 1H), 4.24−4.31 (m, 1H), 5.24 (br s, 1H), 6.49 (d, $J$ = 8.6 Hz, 2H), 7.27−7.35 (m, 7H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) (diastereomer no. 1) $\delta$ 25.43 ($CH_2$), 27.30 ($CH_2$), 60.25 (CHNH), 68.73 ($CH_2O$), 81.29 ($CH_2O$), 99.03 (Ar, *C*CN), 113.31 (Ar, CH), 120.38 (CN), 126.92 (Ar, CH), 127.80 (Ar, CH), 127.87 (Ar, CH), 133.45 (Ar, CH), 138.38 (Ar, *C*CHNH), 150.47 (Ar, CNH); (diastereomer no. 2) $\delta$ 25.61 ($CH_2$), 28.97 ($CH_2$), 61.53 (CHNH), 68.86 ($CH_2O$), 82.66 ($CH_2O$), 99.08 (Ar, *C*CN), 113.43 (Ar, CH), 120.38 (CN), 126.92 (Ar, CH), 127.80 (Ar, CH), 127.87 (Ar, CH), 133.46 (Ar, CH), 140.18 (Ar, *C*CHNH), 150.85 (Ar, CNH). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.86; H, 6.32; N, 10.56.

**Electrochemical Measurement.** The reduction potentials were measured by cyclic voltammetry in a 10 mmol $dm^{-3}$ acetonitrile solution in the presence of 100 mmol $dm^{-3}$ tetraethylammonium perchlorate as a supporting electrolyte with a $Ag/Ag^+$ electrode as a reference. A potentiostat (Hokuto HA-104), a function generator (Hokuto HB-107A), and a cell with platinum electrodes (BAS VC-2) were used for the measurement. All present derivatives gave reversible voltammograms.

**Molecular Orbital Calculation.** The molecular orbital calculations were carried out by CNDO/S[11] and PM3[12] on MATERIA (Teijin System Technology Co.) installed in a Sun SPARC station/10. Details of the CNDO/S calculation are as follows. The geometrical structure for the calculation was optimized beforehand by PM3 with fixed twist angles $\theta_N$ and $\theta_C$. Nishimoto-Mataga approximation was used in the calculations of singlet transitions. The SCF convergence test was carried out on the total energy, and the convergence criterion was 0.00001. The configurations involved in the CI were chosen automatically using the NCONF (number of configurations) configurations of lowest energy and the present NCONF was 60. PM3 calculation for the radical anion was carried out using the UHF method and the structure was optimized from the initial structure with $\theta_N = 55°$ and $\theta_C = 10.3°$.

## Results

### Formation of the Radical Anion upon Photoirradiation of the CN Derivatives in MTHF at 77 K.

Photoirradiation of 5 mmol $dm^{-3}$ 4′-cyanobenzalaniline in MTHF at 77 K for 10 min gave an absorption spectrum with maxima at 440, 473, 515, and 755 nm with shoulders around 400 and 700 nm (Figure 1, solid line). The spectrum was stable over more than 24 h at 77 K, while it rapidly disappeared upon melting of the matrix. This fact indicates that the absorption is due to a transient species which is very short-lived at room temperature. The intensity of the main peak increased with an increase in the photoirradiation time up to the absorbance of 1.0, giving a linear dependence which allows us to determine the formation

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[10] Castellano, J. A.; Goldmacher, J. E.; Barton, L. A.; Kane, S. J. *J. Org. Chem.* **1968**, *33*, 3501.

[11] Ellis, R. L.; Kuehnlenz, G.; Jaffe, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

[12] Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10.

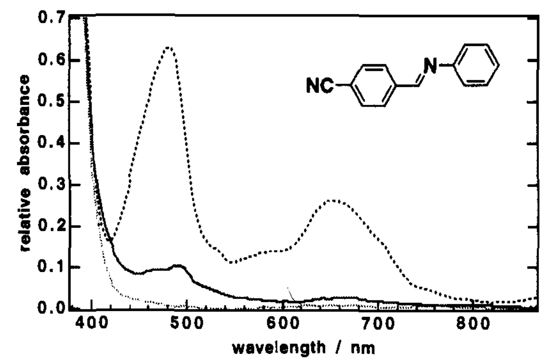
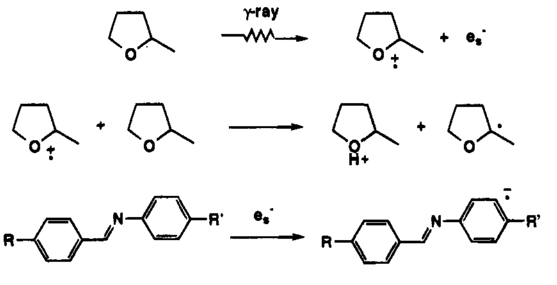


**Figure 2.** Absorption spectra of 5 mmol dm$^{-3}$ 4-cyanobenzalaniline in MTHF at 77 K before irradiation (dotted line), after 10 min of photoirradiation (solid line), and after 5 min of $\gamma$-ray irradiation (dashed line).

efficiency of the species by comparison with other derivatives. Independent $\gamma$-ray irradiation of the 77 K matrix gave an absorption spectrum with maxima at 473 and 755 nm with a shoulder around 700 nm (Figure 1, dashed line). It is well-known that $\gamma$-ray irradiation in MTHF at 77 K induces a one-electron reduction of a solute (eqs 2–4) and the resulting radical anion is efficiently trapped in the low-temperature matrix. The absorption spectrum of the benzalaniline radical anion by this method has been reported.[13]



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Accordingly, we can assign the transient species with absorption maxima at 473 and 755 nm to the radical anion of 4′-cyanobenzalaniline. The small peaks at 440 and 515 nm were not observed upon $\gamma$-ray irradiation. Upon slight annealing of the matrix, these small peaks disappeared with an increase in the main peak at 473 nm. This fact indicates that the absorption bands at 440 and 515 nm are due to a transient species which is thermally converted to the radical anion of the 4′-CN derivative. A similar spectrum was observed upon $\gamma$-ray irradiation of the *syn*-isomer of benzalaniline, which was prepared by photoirradiation (>300 nm) in MTHF at 77 K and trapped in the matrix.[14] Slight annealing of the matrix may induce thermal isomerization of the *syn*-radical anion to the *anti*-radical anion. Accordingly, the transient species with maxima at 440 and 515 nm was assigned to the radical anion of the *syn*-isomer. These results clearly indicate that 4′-cyanobenzalaniline gives the radical anion upon photoirradiation in MTHF at 77 K similarly to $\gamma$-ray irradiation except for minor formation of the *syn*-radical anion.

On the contrary, photoirradiation of the 4-CN derivative in the same manner gave a considerably weak absorption spectrum (Figure 2, solid line) compared to that of the 4′-CN derivative. The spectrum shows absorption maxima at 490 and 660 nm with shoulders around 420 and 460 nm. The shape and the absorption maxima are similar to those of the spectrum independently observed upon $\gamma$-ray irradiation, which has absorption maxima at 480 and 650 nm (Figure 2, dashed line). Accordingly, it is reasonable to assign the transient species to the radical anion of the 4-CN derivative. In this case, formation of the *syn*-radical anion is also possible. However, the peak intensities are too weak to distinguish the *syn*-radical anion from the *anti*-radical anion.

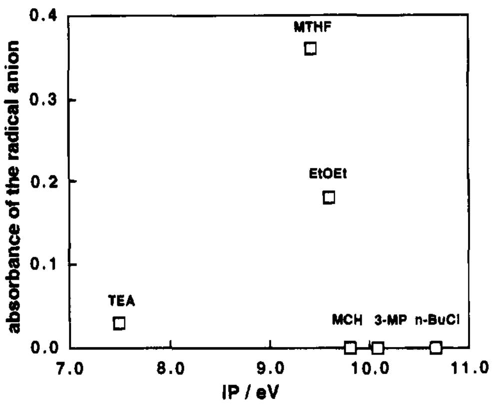

**Figure 3.** Relationship between the absorbance of the radical anion and the ionization potential (IP) of the matrix molecule observed upon photoirradiation of 5 mmol dm$^{-3}$ 4′-cyanobenzalaniline in a series of matrices at 77 K: TEA, triethylamine; MTHF, 2-methyltetrahydrofuran; EtOEt, diethyl ether; MCH, methylcyclohexane; 3-MP, 3-methylpentane; *n*-BuCl, *n*-butyl chloride.

**Effect of Matrix Molecules on the Radical anion Formation of the 4′-CN Derivative.** Radical anion formation of the 4′-CN derivative was also observed upon photoirradiation in diethyl ether at 77 K with rather weak absorbance at the maximum. Photoirradiation of the 4′-CN derivative was carried out in a series of matrix molecules. The 4′-CN derivative showed a slight (1–2 nm) solvent shift in the absorption spectrum, and one can expect almost the same photoexcitation efficiency in a series of solvents. Accordingly, the absorbance of the radical anion observed in a matrix represents the relative yield of the radical anion. Figure 3 shows the relationship between the absorbance of the radical anion at 473 nm and the ionization potential (IP) of the matrix molecule. The radical anion was only produced in a matrix with a low IP. The critical IP giving the radical anion was found to be 9.7 eV. Thus, the dependence of IP suggests that electron transfer from the matrix molecule to the photoexcited state of the 4′-CN derivative induces the radical anion formation. In triethylamine, which is an efficient electron donor, the radical anion was inefficiently produced. Rapid proton transfer from the matrix cation radical may reduce the efficiency of the radical anion trapping.

**Effective Excitation Band for the Radical Anion Formation.** The absorption spectrum of benzalaniline in cyclohexane has four bands as shown in Figure 4. The bands have been named as band I (322 nm), band II (262 nm), band III (236 nm), and band IV (around 220 nm) and assigned on the basis of substituent and solvent effects.[2,5] Band I was assigned to the local $\pi-\pi^*$ transition of Ph$_N$, and band II was assigned to an intramolecular CT transition in which the azomethine group acts as an electron acceptor and Ph$_C$ as an electron donor.[2] Spectral shift of the absorption maxima upon substitution by a strong electron-withdrawing or -donating group does not strongly break the band systems;[5] for example, in the present derivatives, each of the CN derivatives has an absorption spectrum very similar to that of benzalaniline as shown in Figures 7 and 8. That fact allows us to use the conventional expression of the band systems, such as band I and band II, for the present derivatives. Photoirradiation of 4′-cyanobenzalaniline in MTHF at 77 K through a 300-nm cutoff filter was carried out for selective excitation of band I. However, a slight

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(13) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988; p 192.

(14) Ishida, A.; Ito, H.; Takamuku, S. *Chem. Lett.* **1991**, 1537.

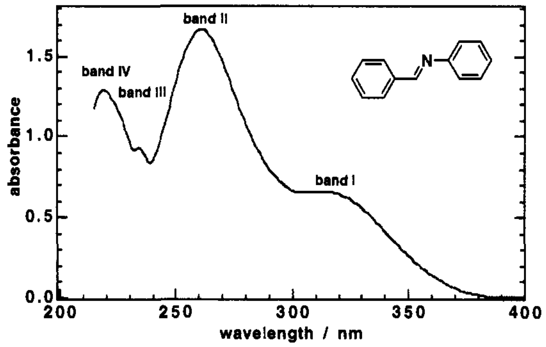
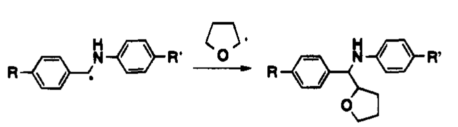


**Figure 4.** Absorption spectrum of 100 $\mu$mol dm$^{-3}$ benzalaniline in *n*-pentane. Characteristic four-band systems, band I (311 nm), band II (261 nm), band III (235 nm), and band IV (around 218 nm), are clearly observed.

increase in the shoulder around 400 nm was observed instead of the radical anion formation. This result indicates that band I is inefficient for the radical anion formation. It has been reported that photoirradiation of benzalaniline at low temperature induces *anti* → *syn* isomerization, and the resulting *syn*-isomer has a weak absorption tail around 400 nm.[15] According to this report, our previous attempt to prepare the *syn*-radical anion was carried out by successive irradiation of UV light (>300 nm) and $\gamma$-rays at 77 K.[14] Photoexcitation of band I is, therefore, proposed to induce *anti* → *syn* isomerization. Because bands III and IV are very weak absorption bands in the short wavelength region, it seems to be difficult to irradiate these bands efficiently under the present experimental conditions. On the basis of these results, we conclude that excitation of band II is responsible for the photoinduced formation of the radical anion. As mentioned in the Introduction, a higher excited state of a benzalaniline derivative is considered to have the unusual property of inefficient conversion to the lowest excited state. For the 4′-CN derivative, excitation of each band induces a corresponding phenomenon. This indicates that the internal conversion is also improbable for the present derivatives.

**Product Formation upon Photoirradiation at Room Temperature.** One should point out here that band II is also an effective excitation band for the photochemical THF addition of the 4′-CN derivative at room temperature.[9,16] The adduct formation was proposed to proceed via the radical anion, and the mechanism was supported by a deuterium kinetic isotope effect[9,16] and an electrolyte effect.[16] Upon photoinduced electron transfer from THF to a benzalaniline derivative, a pair of a THF cation and the radical anion is formed. A THF cation gives an oxonium-type ion and a tetrahydrofuran-2-yl radical by the ion–molecule reaction similarly to that of the MTHF cation shown in eq 3. The former reacts with the radical anion, giving the benzyl-type radical[14] (eq 5), and the latter gives the 1:1 adduct by recombination with the benzyl-type radical[14] (eq 6). Once the radical anion is formed in THF by the photoinduced electron transfer reaction or by $\gamma$-ray irradiation, therefore, it gives the adduct in a high yield at room temperature.[14] In the present system, the radical anion, which is isolated in a matrix at 77 K, is proposed to give the adduct by successive reaction upon melting of the matrix similarly to the reaction at room temperature. In fact, the 1:1 MTHF adduct was observed by GC–MS analysis after melting of the matrix.



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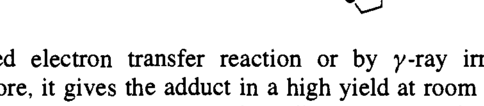

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**Laser Flash Photolysis at Room Temperature.** Laser flash photolysis of the 4′-CN derivative was attempted in THF at room temperature. The fourth harmonic of a Q-switched Nd:YAG laser is expected to excite band II at 267.2 nm efficiently. Unfortunately, however, we could not detect any transient absorption of expected species such as the radical anion and the benzyl-type radical which is generated by protonation of the radical anion. The radical anion is efficiently trapped in a 77 K matrix; moreover, the photoirradiation at room temperature gave the adduct in a high yield via the radical anion as described above. The results suggest that the successive reactions to the electron transfer, i.e., a protonation of the radical anion (eq 5) and a recombination of the radicals (eq 6), very rapidly occur. Thus, the lifetime of the species seems to be too short to permit its detection by use of a nanosecond laser flash photolysis system.

**Radical Anion Formation upon Photoirradiation of Other Derivatives.** Because the laser flash photolysis was unsuccessful, the formation efficiency of the radical anion was determined by use of a low-temperature matrix measurement. For comparison of the radical anion formation in a series of derivatives upon photoirradiation in MTHF at 77 K, the absorbance of the radical anion at a main peak around 480 nm was used as a measure of the efficiency. We confirmed the accuracy of the determination method as follows. First, the molar extinction coefficient of the radical anion should be determined for the series of derivatives. Upon $\gamma$-ray irradiation in MTHF at 77 K with the same dose, the series of derivatives gave absorption spectra of the radical anions with a similar shape and absorbance at the maximum around 480 nm. The same dose of $\gamma$-ray irradiation yields the same amount of solvated electrons with a sufficient reduction potential for a one-electron reduction of the present derivatives; therefore, the radical anions were produced in almost the same yield. These facts indicate that the radical anions have similar molar extinction coefficients at the absorption maxima around 480 nm. Second, the photoexcitation efficiency should be the same for the series of derivatives. Fortunately, the present derivatives have absorption spectra with a similar shape and absorbance at the maxima, and that fact enables us to photoirradiate all derivatives with similar efficiency using the white light source. Third, the yield of the radical anion should linearly increase with increased photoirradiation time. For the 4′-CN derivative, which efficiently gave the radical anion, the main peak at 473 nm increased with increased photoirradiation time up to an absorbance of 1.0. The linear dependence allows us to determine the efficiency of the radical anion formation by measurement of the absorbance. On the basis of these facts, we can determine the relative yield of the radical anion upon photoirradiation by comparison of the absorbance at the maximum around 480 nm for the series of derivatives.

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(15) Kobayashi, M.; Yoshida, M.; Minato, H. *Chem. Lett.* **1976**, 185.

(16) The detailed results of the photochemical THF adduct formation will be published in the near future. The deuterium kinetic isotope effect on the adduct formation was determined by the MS peak ratio of the product obtained by the photoirradiation in a mixture of THF and THF-$d_8$. The isotope effect for the 4′-CN derivative was $k_H/k_D = 2.4$, which was considerably smaller than that for the 4-MeO derivative ($k_H/k_D = 5.6$). The adduct yield for the 4′-CN derivative at unit time increased 1.6–2.3 times upon addition of an electrolyte (20 mmol dm$^{-3}$) such as $NaClO_4$, $Mg(ClO_4)_2$, and $Et_4NClO_4$. On the other hand, the acceleration effect on the reaction of the 4-MeO derivative was negligible. The photoirradiation of the 4′-CN derivative in triethylamine and diethyl ether at room temperature also gave new GLC peaks, which were considered to be due to the adducts. The isolation and characterization are in progress.

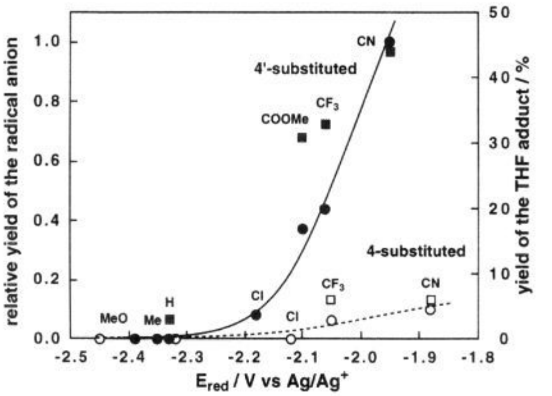
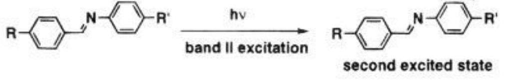
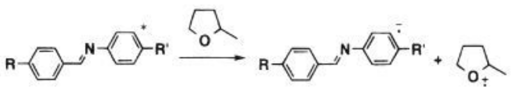


**Figure 5.** Absorbance of the radical anion at the peak around 480 nm observed upon photoirradiation in MTHF at 77 K (average for four runs) plotted versus the reduction potentials for the series of 4- (open circles) and 4′-substituted (closed circles) derivatives. The yields of the solvent adducts upon photoirradiation of the 4- (open squares) and the 4′-substituted (closed squares) derivatives in THF at room temperature are also plotted (right axis).

In Figure 5, the absorbance average for four runs and the yield of a 1:1 THF adduct upon photoirradiation at room temperature are plotted versus the reduction potentials for the series of 4- and 4′-substituted derivatives. Three important features are summarized from Figure 5 as follows: (1) The yield of the radical anion highly depends upon the reduction potential of the benzalaniline derivative, and the critical reduction potential giving the radical anion is proposed to be −2.2 V vs Ag/Ag$^+$. This suggests that electron transfer from a matrix molecule to the second photoexcited state of a benzalaniline derivative (eq 8) induces the radical anion formation. The result is consistent with the IP effect that only a matrix molecule with a lower IP than 9.7 eV gave the radical anion. (2) For the series of electron-deficient derivatives efficiently giving radical anions, the absorbance corresponds to the yield of the 1:1 THF adduct, which is a final product of the radical anion as described above. Thus, the correspondence between the absorbance and the yield of the adduct indicates that the yield of the trapped radical anion, i.e., the absorbance, correctly represents the yield of the electron transfer reaction. It is reasonable to assume that the yield of the electron transfer reaction corresponds to the electron transfer rate. Accordingly, the absorbance is expected to represent the electron transfer rate with sufficient accuracy. (3) There is a striking difference between the yield of the radical anion for the series of 4- and 4′-substituted derivatives, and 4′-substituted derivatives more efficiently afforded the radical anions than 4-substituted derivatives. This fact indicates that the electron transfer efficiency depends not only on thermodynamics but also on the structural features giving the highly site-specific substituent effect.



(7)



(8)

The present experimental results are summarized as follows: (1) a benzalaniline derivative with an electron-withdrawing substituent gave the radical anion upon photoirradiation in MTHF at 77 K, (2) the effective excitation band was band II around 260 nm, giving the second excited state, (3) the efficiency of the radical anion formation depended upon the IP of the matrix molecule, the reduction potential of the benzalaniline derivative, and the position of the substituent, (4) the yield of the radical anion corresponded to that of the adduct obtained by the photochemical reaction at room temperature, and (5) a low-temperature matrix efficiently trapped a short-lived species of a photochemical reaction which could not be detected by a nanosecond laser flash photolysis at room temperature.

## Discussion

**Estimation of the Free Energy Change of the Photoinduced Electron Transfer Reaction.** On the basis of these experimental results, we estimate that the second photoexcited state of the benzalaniline derivative undergoes electron transfer reaction from MTHF, resulting in the formation of the radical ion pair (eq 8). It is widely known that the free energy change in the photoinduced electron transfer reaction depends upon the reduction potential of the acceptor (a benzalaniline derivative), the oxidation potential of the donor (a matrix molecule), the excitation energy (energy of band II), and the Coulombic factor (eq 9).[17,18] In the case of the 4′-CN derivative, for example, the reduction potential is −1.95 V vs Ag/Ag$^+$ and the excitation energy of band II ($\lambda_{max}$ = 268.8 nm in THF) is 4.61 eV. Oxidation potentials of THF and MTHF are not available in the literature. It has been reported that ionization potentials of molecules show a linear relationship with the oxidation potentials (eq 10),[19] and we can estimate the oxidation potential of MTHF at 2.34 V vs Ag/Ag$^+$. From these data, one can estimate the free energy change to be −0.32 eV (−31 kJ mol$^{-1}$), neglecting the Coulombic factor which is usually less than 8 kJ mol$^{-1}$. Accordingly, the electron transfer reaction from the second excited state of the 4′-CN derivative from MTHF is sufficiently exothermic at room temperature. A considerable increase in $\epsilon$ at low temperature seems to increase the Coulombic factor; however, the efficient trap of the radical anion indicates that the electron transfer is still exothermic at 77 K.

$$\Delta G = E_{ox} - E_{red} - \Delta E + c \tag{9}$$

$$E_{1/2}/(\text{V vs Ag/Ag}^+) = 0.89(\text{IP}) - 6.04 \tag{10}$$

The critical ionization potential of the matrix molecule giving the radical anion for the 4′-CN derivative was found to be 9.7 eV as shown in Figure 3. The free energy change at this point is −0.067 eV (−6.0 kJ mol$^{-1}$) which is close to zero upon consideration of the Coulombic factor. Photoexcitation of band I ($\lambda_{max}$ = 328 nm in THF) was ineffective for the radical anion formation as described above. The excitation energy is only 3.78 eV, and the estimated free energy change is 0.51 eV (49 kJ mol$^{-1}$), suggesting inefficient electron transfer. Benzalaniline, which has a more negative reduction potential (−2.33 V vs Ag/Ag$^+$) than the 4′-CN derivative (−1.95 V), gave no radical anion. In this case, the free energy change upon photoexcitation of band II is estimated to be −0.06 eV (−5.7 kJ mol$^{-1}$), also suggesting inefficient electron transfer. On the contrary, a similar estimation for the 4-CN derivative gave a free energy change of −0.32 eV (−31 kJ mol$^{-1}$), from which one can expect efficient electron transfer. However, the actual radical anion formation was considerably less efficient than that of the 4′-CN derivative. A similar difference between the yield of the radical anion and the estimated free energy change was observed for the series of 4-substituted derivatives with an

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[17] Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.

[18] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[19] Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

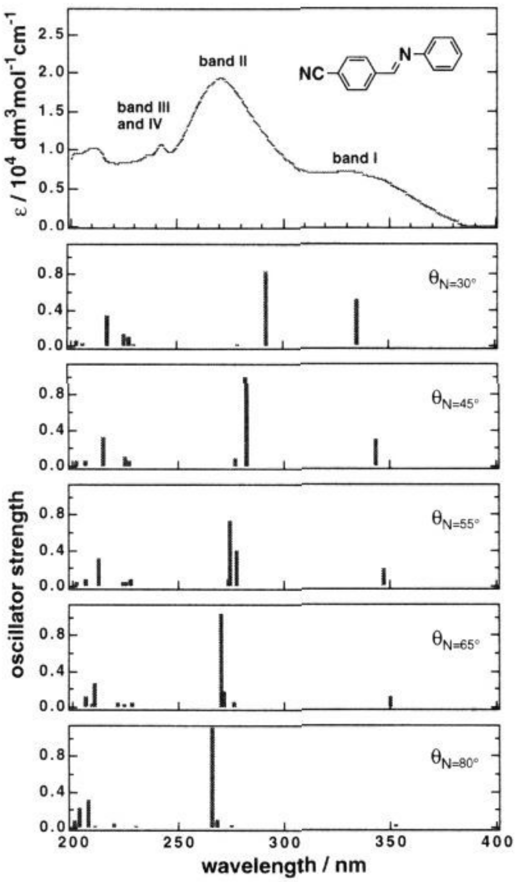

**Figure 6.** Comparison of the absorption spectrum observed in cyclohexane and calculated spectral patterns of 4-cyanobenzalaniline for varying degrees of the twist angle $\theta_N$.

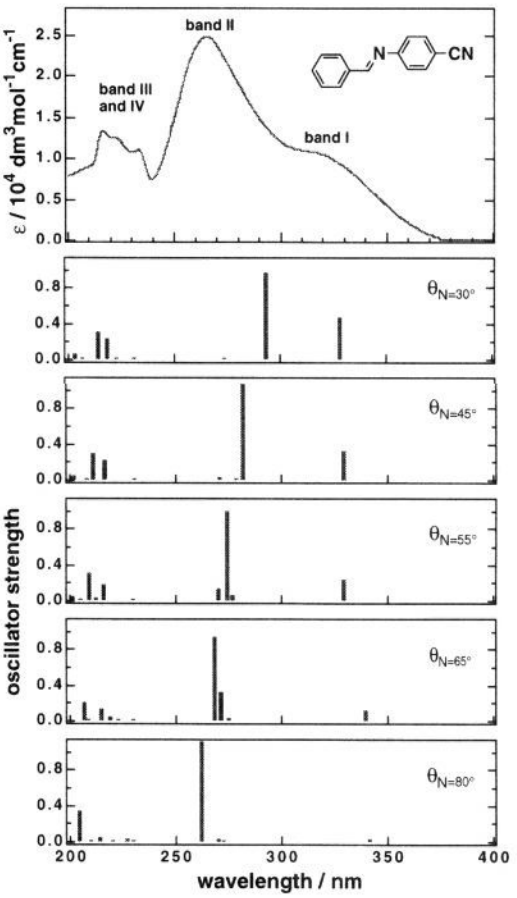

**Figure 7.** Comparison of the absorption spectrum observed in cyclohexane and calculated spectral patterns of 4′-cyanobenzalaniline for varying degrees of the twist angle $\theta_N$.

electron-withdrawing substituent. As described above, both of the CN derivatives have similar band systems as shown in Figures 6 and 7. These facts imply that a positional change of the substituent does not result in a considerable difference in the energy level of the lower unoccupied orbitals even though a split occurs in the conjugated system. Thus, one has to consider that the efficiency of the radical anion formation highly depends upon a factor other than the excitation energy and reduction potential of the derivatives leading to the site-specific substituent effect. For example, the magnitude of a Coulombic interaction between the photoexcited state and a matrix molecule depends upon the position of the substituent. The interaction will be discussed with the results of the MO calculation.

**Intermolecular CT Interaction of a Benzalaniline Derivative with MTHF in the Ground and Photoexcited States.** Similar photoinduced formation of a solute radical anion in MTHF at 77 K has been reported only in the cases of extremely electrophilic molecules such as tetracyanobenzene and pyromellitic dianhydride.[20] These molecules efficiently produce an intermolecular CT complex with MTHF in the ground state, and appearance of an intense intermolecular CT band in the longest wavelength region of the absorption spectrum indicates that the lowest $S_1$ is the intermolecular CT state. Photoinduced radical anion formation of these extremely electrophilic molecules in MTHF at 77 K is due to photoexcitation of the intermolecular CT complex.[20] On the contrary, we could not observe an intermolecular CT band of the present benzalanilines with MTHF even for the CN derivatives. This fact indicates that the electrophilicity of the present derivative is insufficient for the ground state intermolecular CT with MTHF. Intermolecular CT of benzalaniline with small polar molecules has been reported only for strongly polar derivatives.[4,21−23] 4-Methoxy-4′-nitrobenzalaniline[4] and 5-(dimethylamino)-3,3-dimethyl-2-(*p*-nitrophenyl)-3*H*-indole[21,22] produced a weak complex with ethanol and acetonitrile in the ground state, leading to a remarkable red shift of the absorption maximum.[24] Fluorescence studies of these derivatives indicated formation of an exciplex with these small polar molecules stabilized by weak intermolecular CT interaction.[21,22] Because the present benzalanilines showed a slight (1 or 2 nm) red shift of the absorption maximum upon addition of THF in cyclohexane, it is difficult to expect strong ground state interaction with MTHF. It may

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(20) Kimura, K. *Reviews of Chemical Intermediates*; Verlag Chemie: Weinheim, Germany. 1979; Vol. 2, p 321.

(21) Belletete, M.; Lessard, G.; Durocher, G. *Can. J. Spectrosc.* **1986**, *31*, 89−94.

(22) Belletete, M.; Lessard, G.; Richer, J.; Durocher, G. *J. Lumin.* **1986**, *34*, 279−286.

(23) Belletete, M.; Durocher, G. *J. Phys. Chem.* **1989**, *93*, 1793−1799.

(24) Belletete et al. reported in ref 12 that a strongly polar benzalaniline derivative shows a shift of the absorption bands, keeping the band systems upon changing the solvent polarity instead of an intense CT band appearing with solvents. They tried to estimate the dipole moment in the ground state by a vector model (ref 30) and those in the photoexcited states by Mataga and Lippert's treatment (refs 31 and 32). The results are summarized as follows: (1) the dipole moment for a substituted benzalaniline considerably changes in the second excited state compared to that in the ground state, (2) the intramolecular CT character of band II arises from the presence of a substituent, and (3) a change of the dipole moment upon photoexcitation will strongly reflect the position of the substituent. We also tried to estimate the dipole moments of the present derivatives in the second photoexcited state by a similar manner. However, we could not observe such a strong solvent shift even for the cyano derivatives, which seem to be the most polar molecules in the series.

**Table 1.** Properties of Benzalaniline and the 4- and 4′-Substituted Derivatives in the Ground and Second Photoexcited States[a]

| substituent | | | | | | | charge density (CD) of the anil groupf | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | R′ | anion yield[b] | $\theta_N$[c] | $E_{red}$[d]/V | $\mu_z$ | $\mu_z$**[e] | $CD_N$ | $CD_N$** | $\delta CD_N$ | $CD_C$ | $CD_C$** | $\delta CD_C$ |
| H | H | 0 | 45 | −2.33 | 1.5 | 0.3 | −0.301 | −0.254 | 0.047 | 0.120 | −0.011 | −0.131 |
| $CF_3$ | H | 0.05 | 50 | −2.05 | −2.5 | −7.7 | −0.289 | −0.240 | 0.049 | 0.118 | 0.023 | −0.095 |
| H | $CF_3$ | 0.45 | 55 | −2.06 | 4.3 | 3.4 | −0.286 | −0.277 | 0.009 | 0.113 | −0.018 | −0.131 |
| CN | H | 0.1 | 55 | −1.88 | −3.2 | −7.9 | −0.271 | −0.275 | 0.004 | 0.103 | 0.036 | −0.067 |
| H | CN | 1.0 | 55 | −1.95 | 6.6 | 4.6 | −0.286 | −0.257 | 0.043 | 0.117 | 0.017 | −0.100 |

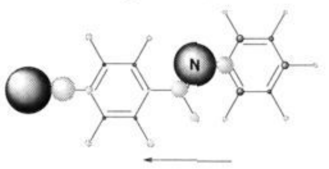
[a] The double asterisk means the value upon photoexcitation of band II. [b] Relative absorbance of the radical anion averaged for four runs normalized for the 4′-CN derivative. [c] Twist angle estimated by comparison of the calculated spectral pattern with the observed absorption spectrum. [d] Reduction peak potential of cyclic voltammetry vs the Ag/Ag$^+$ electrode. [e] Dipole moments were calculated by CNDO/S. The $z$ axis is consistent with the C=N bond. The plus sign indicates that the dipole moment is directed toward $Ph_C$ from $Ph_N$. [f] Net charge density on the anil carbon and nitrogen atoms in the ground and second excited states calculated by CNDO/S. $\delta CD_N$ and $\delta CD_C$ are the differences between the ground and second excited states.

be due to a considerably smaller dipole moment and electrophilicity of the present benzalaniline than those of the reported derivatives. Accordingly, one can expect strong Coulombic interaction between the present benzalaniline and the matrix molecule only in the photoexcited states.[25]

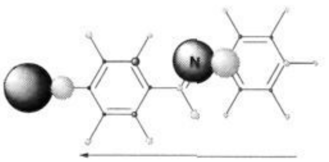
**CNDO/S Calculation for the Benzalaniline Derivative.** CNDO/S calculation for benzalaniline has been reported.[26] Comparison of the observed absorption spectrum and calculated oscillator strength for varying degrees of the twist angle $\theta_N$ indicates that the calculation correctly estimates the twist angle in the ground state. For example, the estimated twist angle for benzalaniline by this method (55°)[26] is very close to that in the gas phase (52°) independently determined by the electron diffraction study.[27] On the basis of the reported method, we tried to estimate the ground state geometries for the present derivatives. The twist angle $\theta_C$ was fixed at 10.3°, which is the same angle as that for crystalline benzalaniline,[28] because $\theta_C$ did not affect the spectral pattern with its variation from 0° to 10.3° in the preliminary calculations. The calculated results for the spectral patterns at various $\theta_N$ angles are illustrated in Figures 6 and 7 together with the observed absorption spectra in $n$-pentane.

For both 4- and 4′-CN derivatives, the calculation with the twist angle $\theta_N$ of 50−60° can well reproduce the observed spectrum. Accordingly, we estimate the twist angles at $\theta_N$ = 55°. The good agreement between the calculated and observed absorption spectra suggests high accuracy of the electron density estimation for the photoexcited states even by the semiempirical calculation. Using the geometries, we estimated the dipole moments and net atomic charges of the benzalanilines in the ground state and second photoexcited state, which is the key excited state for the radical anion formation. The calculation results for benzalaniline, the CN derivatives, and the $CF_3$ derivatives are summarized in Table 1. The dipole moments of benzalaniline in the ground and second excited states are consistent with the reported values.[5,29] The dipole moments and the net atomic charges for the 4- and 4′-CN derivatives in the ground and second photoexcited states are visualized in Figure 8.

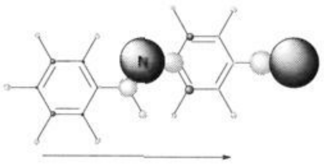
4-CN derivative ground state



4-CN derivative second excited state



4′-CN derivative ground state



4′-CN derivative second photoexcited state

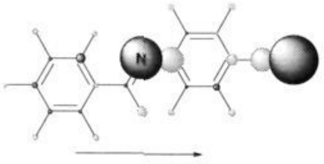


**Figure 8.** Charge density maps of the 4- and 4′-CN derivatives in the ground state and upon photoexcitation of band II calculated by CNDO/S. The size of the sphere represents the magnitude of the charge density on the atom. Black and gray colors represent negative and positive charges, respectively. The arrow shows direction and magnitude of the dipole moment on the $z$ axis, which is consistent with the C=N bond.

The CNDO/S calculation results enable us to find a considerable difference in the dipole moments and charge distributions in the ground and second photoexcited states between the 4′- and 4-substituted derivatives. First, the 4′-substituted derivative has a dipole moment with a direction opposite that of the 4-substituted derivative in both the ground and second photoexcited states. Second, the dipole moments of the 4-substituted derivatives considerably increase upon the second photoexcited state, while those of the 4′-substituted derivatives decrease. These calculation results are consistent with the reported assignment of band II to an intramolecular CT excited state.[2] Benzalaniline caused a small change in the dipole moment upon photoexcitation of band II. This indicates that the considerable difference in the dipole moment and charge distribution for the

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(25) Unfortunately, it is difficult to use fluorescence measurements for quantitative determination of the exciplex formation because the fluorescence intensities of the present derivatives were very weak. The molecular orbital calculation is, therefore, the only way to predict the electronic properties upon photoexcitation of band II.

(26) Akaba, R.; Tokumaru, K.; Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1993.

(27) Traetteberg, M.; Hilmo, I.; Abraham, R. J.; Ljunggren, S. *J. Mol. Struct.* **1978**, *48*, 395.

(28) Bürgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747.

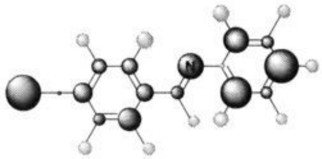
(29) Gaouck, V. A.; Lefevre, R. J. W. *J. Chem. Soc.* **1938**, 741.

(30) Pitea, D.; Grasso, D.; Favini, G. *J. Chem. Soc. B* **1971**, 2290.

(31) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690; *ibid.* **1956**, *29*, 465.

(32) Lippert, E. *Z. Naturforsh.* **1955**, *10a*, 541; *Z. Elektrochem.* **1957**, *61*, 962.

**4-CN derivative radical anion**



**4'-CN derivative radical anion**

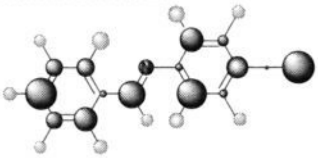


**Figure 9.** Charge density maps of the radical anions of 4- and 4′-CN derivatives calculated by PM3. The size of the sphere represents the magnitude of the charge density on the atom. Black and gray colors represent negative and positive charges, respectively.

substituted benzalanilines arises from the presence and the position of a substituent. For example, as shown in Figure 8, although the dipole moment of the 4′-CN derivative decreases in the second photoexcited state, the positive charge is efficiently localized on the $Ph_N$. On the contrary, the positive charge of the 4-CN derivative in the second photoexcited state is dispersed in the whole molecule, while the dipole moment considerably increases. On the basis of these contrast calculation results, the considerably different reactivities between the two derivatives are easily predicted. However, it is difficult to have a mechanistic explanation for the site-specific substituent effect at present, and we would propose a possibility of exciplex formation between the second photoexcited state and MTHF which affects the reactivities. Upon PM3 calculation for the radical anion which is the "product" of the electron transfer reaction, the negative charge delocalizes on the whole molecule for both radical anions as shown in Figure 9. Once the electron transfer is completed, accordingly, both derivatives have similar Coulombic interaction between the radical anion and the MTHF cation, giving the radical anions with similar yields. Therefore, the difference in the radical anion yields is due to the difference in the CT interaction of the exciplex estimated from the Coulombic interaction between the second photoexcited state and MTHF. Although the second photoexcited state of a 4′-substituted derivative has a small dipole moment, the positive charge is efficiently localized on the $Ph_N$, which may induce strong Coulombic interaction with MTHF. Thus, a tight complex is formed, resulting in an efficient formation of a radical ion pair. On the contrary, a 4-substituted derivative has a large dipole moment; however, the positive charge is dispersed in the whole molecule. This allows rather weak interaction with MTHF, leading to an inefficient electron transfer.

## Conclusion

An electron-withdrawing substituent on the 4- or 4′-position of benzalaniline efficiently assists the intramolecular charge transfer character of the second photoexcited state. Only in the cases of the 4′-substituted derivatives, the Coulombic interaction between the second photoexcited state and a small polar molecule such as MTHF and diethyl ether efficiently yields the radical anion. A large dipole moment, which is seemingly expected to give a tight complex, is not always favorable for the successive electron transfer or for the efficient separation of the radical ion pair as in the cases of the 4-substituted derivatives. The present results suggest that one should consider the local charge distribution instead of the physical characteristics of the whole molecule such as the reduction potential and the dipole moment to assume the reactivity of the photoexcited states of a large polar molecule. Moreover, the present results indicate that a low-temperature matrix measurement is still a powerful tool for photochemistry involving rapid electron transfer.

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