The Class II/III Transition Electron Transfer on an Infrared Vibrational Time Scale for N,N'-Diphenyl-1,4-phenylenediamine Structures

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Intramolecular electron transfer (ET) within the class II/III transition for the mixed-valence state of N, N'diphenyl-1,4-phenylenediamine (PDA) derivatives which were substituted in the center or the outer phenyl ring and N,N'-diphenylbenzidine (BZ) was examined. Each compound showed two reversible redox couples. The splitting of the redox waves, ΔE , is related to the interaction intensity between redox sites. The introduction of a substitutent into the central phenylene ring of the PDAs resulted in a decrease in ΔE . A similar result was noted for the expansion of the distance between the redox centers such as in BZ. In opposition, the ΔE of N,N'-bis(2,6-dimethylphenyl)-1,4-phenylenediamine (2,6-DMPDA) as a compound with substituents introduced into the outer phenyl rings was spread. The mixed-valence state of these compounds also exhibited an intervalence charge transfer (IV-CT) band in the near-IR region which provided the determination of the Marcus reorganization energy (λ), the electron coupling (V), the thermal ET barrier (ΔG^*), and the electrontransfer rate (k_{th}) using the Marcus-Hush theory. We first confirmed the electron-transfer rate of PDA derivatives in the class II/III transition state by two methods. The ν (N-H) stretching vibrational spectra of the mixed-valence states were analyzed by a Bloch-type equation analysis using variable-temperature IR spectra measurements which were to be in good agreement with the those obtained from the Marcus-Hush theory. On the basis of this approach, the electron-transfer rate of PDA was determined to be $8.2 \times 10^{11} \text{ s}^{-1}$ at 298 K, yielding $\Delta G^{\ddagger} = 420 \text{ cm}^{-1}$ (the activation free energy from the Eyring plot) for the underlying process.

Introduction

The electron-transfer (ET) process is fundamentally one of the most important processes in chemical reactions.¹ Especially, the construction of a fast ET system² is considerably important for the development of functional molecules possessing properties of electrical conductivity,³ ferromagnetism,⁴ and charge separation.⁵ *N*,*N'*-Diphenyl-1,4-phenylenediamine⁶ (PDA), which is a redox unit of polyaniline, as one of the most well-known conducting polymers⁷ possesses a stable two-electron redox couple in the presence of a Lewis acid. However, there have been no reports on the physicochemical properties, such as electron transfer and IV-CT in the mixed-valence (MV) state of the polyaniline unit (e.g., the relationship between the substitution effect and the conductivity of the polyaniline based on IV-CT).

Organometallic and inorganic compounds, with MV states, e.g., such as the Creutz-Taube ion⁸ and 1,4-pyrazine-bridged ruthenium cluster complexes,⁹ have been analyzed using the Marcus—Hush theory.¹⁰ The first direct investigation of ET rate analysis was done by Ito and Kubiak et al. using a Bloch-type equation which was independent of the major problems of the MV state in class II/III transitions, such as the exact distance between the redox centers due to charge delocalization or the nuclear frequency factor (ν_n).⁹ Recently, many studies of organic compounds in the MV state^{11–14} have been reported by Nelsen et al. using both the Marcus—Hush theory and ESR measurements.¹¹ The discussion of ET has been expanded to the class II/III transition state by Lambert et al. by simple IV-CT analysis using the Marcus–Hush theory.¹² To resolve these problems, we employed IR spectra analysis, which is suitable for confirmation of the results of IV-CT analysis, because the time scale of the ET rate in the class II/III transition state reaches picoseconds.¹⁵

We herein report the analysis of the electron-transfer rate of monocation radicals formed at the amine sites of PDA derivatives using the Marcus—Hush theory in order to elucidate the substituent effect at the outer *N*-phenyl or the inner phenylene ring. The ET rate constant was determined by two methods. One was IV-CT band analysis using the Marcus—Hush theory, and the other was the ν (N—H) stretching absorption observed in the temperature range from 193 to 298 K, which is analyzed with regard to the ET rate by simulated dynamic effects (Blochtype equations).¹⁶ The important advantage of this IR method lies in the independence from the concentration of the MV state in the solution and the distance between two redox centers in the MV compounds and an exact nuclear frequency factor.

IV-CT states are classified as classes I, II, and III on the basis of the electronic coupling intensity between redox sites.¹⁷ The fastest electron transfer takes place in the class II/III transition state.^{2c,12a,} No IV-CT band is observed for class I because the ET coordinates are completely localized on only the diabatic surfaces. For class II, the IV-CT absorption band is usually observed in the near-IR region as being distorted from a Gaussian shape in the low-energy region¹⁷ due to the cutoff around the electric coupling. For class III, the electron coupling is so strong that the redox centers are completely delocalized

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CHART 1. Chemical Structures of PDA Derivatives with Atom Labeling



in the system, and collapsing of IV-CT absorption symmetry is observed.^{2c,12a} In this paper, the configuration of the IV-CT band was compared by introducing a substituent into the inside or the outside phenyl ring of PDA. We found that N,N'-bis(2,6-dimethylphenyl)-1,4-phenylenediamine (2,6-DMPDA), which was substituted in the outer phenyl rings, showed a redox center completely delocalized class III property on the basis of the solvent effect even though PDA was classified as a class II/III transition compound.

Results and Discussion

The set of molecules that have a *p*-phenylenediamine moiety twisted by the substituents is shown in Chart 1. The pphenylenediamine moiety was chosen so as to ensure a reversible two-redox reaction with strong interaction between the N atoms as redox centers and an accurate N-H stretching vibration spectrum around 3400 cm⁻¹. The syntheses of the compounds are described in the Experimental Section and in previous reports18 and were accomplished by palladiumcatalyzed C-C or C-N cross-coupling or the dehydration of ^tBu-, methyl-, or bromo-substituted benzoquinone and aniline in the presence of TiCl₄ for the *p*-phenylenediamine moiety. Because the electronic interaction intensities between the redox centers are influenced dramatically by the twist of the highest occupied molecular orbital (HOMO) on the N atoms, we synthesized a series of compounds that have substitutions on the inner or outer phenyl rings.

Electrochemistry. The cyclic voltammograms (CV) of innerphenyl-modified PDA derivatives show two reversible redox processes in dichloromethane containing 0.2 M tetrabutylammonium perchlorate (TBAP). The CV of PDA and PDA-Br as typical examples are shown in Figure 1. In the one-electron oxidative state between the first and second redox potentials, the cation radical is formed, and a stable IV-CT between two amine sites takes place. All electrochemical results are shown in Table 1. The first (E°_{1}) and the second (E°_{2}) half-wave potential and the redox potential splitting (ΔE) of nonsubstituted PDA are 0.14, 0.67 (vs Ag/Ag⁺), and 0.53 V, respectively. The E°_{1} , E°_{2} , and ΔE of PDA-Ph and PDA-Th, which are the π -conjugated aryl-substituted PDA derivatives, are 0.27 V, 0.63 V, 0.36 V and 0.33 V, 0.55 V, 0.22 V, respectively. For PDA-Me, PDA-'Bu, and PDA-Br, which are nonconjugated-groupsubstituted PDA derivatives, the E°_{1} , E°_{2} , ΔE are 0.16, 0.57, 0.41; 0.27, 0.48, 0.21; and 0.48, 0.71, 0.23, respectively. For BZ, which has a different distance between the two redox



Figure 1. Cyclic voltammograms of 1.0 mM PDA (solid curve) and 1.0 mM PDA-Br (dotted curve) in CH_2Cl_2 containing 0.2 M TBAP. Scan rate: 0.1 V/s.

TABLE 1:	Electrochemical	Data for	PDA	Derivatives
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$compd^a$	$E^{\circ}{}_{1}{}^{b}$ [V]	$E^{\circ}{}_{2}{}^{c}$ [V]	$\Delta E^d [V]$	$K_{ m co}{}^e$
PDA	0.14	0.67	0.525	7.4×10^{8}
PDA-Me	0.16	0.57	0.412	9.1×10^{6}
PDA-Ph	0.27	0.63	0.360	1.2×10^{6}
PDA-Br	0.48	0.71	0.231	$8.0 imes 10^3$
PDA-Th	0.33	0.55	0.219	5.0×10^{3}
PDA- ^t Bu	0.27	0.48	0.213	4.0×10^{3}
BZ	0.35	0.55	0.204	2.8×10^{3}

^{*a*} Cyclic voltammograms recorded in CH₂Cl₂ containing 0.2 M TBAP at ca. 298 K. ^{*b*} 0/1+ couple vs Ag/Ag⁺. ^{*c*} 1+/2+ couple vs Ag/Ag⁺. ^{*d*} $E^{\circ}_{2} - E^{\circ}_{1}$. ^{*e*} $K_{co} = 10^{(\Delta E/0.0592)}$.

centers, the E°_{1} , E°_{2} , ΔE are 0.35, 0.55, 0.20. In the case of PDA, the ΔE is 0.53 V, in which the comproportionation constant¹⁹ (K_{co}) is calculated to be 9.6 \times 10⁸. A large K_{co} indicates a high stability of the monocation radical state, which is estimated to be a MV state (+1 and 0 state). The relationship between the electrochemical value of ΔE and the electronic coupling constant (V) has been discussed.²⁰ In our case, a monotonically increasing relationship was found except for PDA- ${}^{t}Bu^{\bullet+}$. We simply treated the electrochemical processes of PDA derivatives as an EE process ("electron transfer" is abbreviated as E) because the solvent donor number of dichloromethane is sufficiently lower, and in dichloromethane with 0.2 M TBAP, the second reversible redox couple was confirmed without proton transfer. Generally, in the case of the two-step redox reactions of PDA derivatives, the redox potentials and the ΔE are dependent not on the Hammett rule such as a substitution effect (electron-donating or -withdrawing nature), but on the Nernst equation. The magnitude of ΔE is enlarged by an electronic interaction such as Columbic repulsion through the π -linked group but is made smaller by a conformational change after electron removal based on steric hindrance and the solvent dipole moment, resulting in the solvent reorganization energy. When assuming that the series of the measurements of the redox potentials of PDA derivatives is under the same conditions, the twist of the orbital on the N atoms makes the magnitude of ΔE small.

Spectroelectrochemistry. The MV states of PDA derivatives were also confirmed by spectroelectrochemical (SEC) analysis in dichloromethane containing 0.2 M TBAP. In the case of PDA, the absorption band attributed to the monocation radical state (ν_{max}) appears at 14 100 cm⁻¹ on applying a potential from 0.1 to 0.35 V (vs Ag/Ag⁺), and the absorption band disappeared on applying a potential at ca. 0.8 V (vs Ag/Ag⁺), at which potential the monocation radical species are further oxidized to the dication (Figure 2). The ν_{max} values of PDA-Ph, PDA-Th, PDA-Me, PDA-Fu, PDA-Br, and BZ are at 13 900, 13 100, 14 800, 15 200, 13 300, and 8730 cm⁻¹, respectively (Table 2).



Figure 2. Electronic absorption spectral data for PDA in neutral (dotted curve), one-electron oxidized (solid curve), and two-electron oxidized (dashed curve) state. Their potentials are 0.0, 0.3, and 0.8 V (vs Ag/Ag⁺), respectively. Light path length: 1.0 mm; concentration: 1.0 mM PDA, 0.2 M TBAP in CH₂Cl₂ at ca. 298 K.

Figure 3 shows the IV-CT bands of PDA^{•+} and PDA-Br^{•+} as typical spectra and their fitted Gaussian curves. The resulting bands are not symmetrical and possess a Gaussian shape in the high-energy region, but the wave in the low-energy side did not overlap with a Gaussian band shape. The reason why the IV-CT band for the class II/III transition state is cut off at the low-energy site was described by Lambert et al. in ref 12. These results support the idea that the band is estimated to be an IV-CT based on a MV state classified as a class II/III transition. On the basis of the classical Marcus—Hush theory, electronic coupling V (in cm⁻¹) has been calculated by deconvolution of the IV-CT band spectra as follows:¹⁰

$$V = \frac{2.06 \times 10^{-2}}{r} \sqrt{\tilde{\nu}_{\max} \tilde{\nu}_{1/2} \epsilon}$$
(1)

where $\tilde{\nu}_{\text{max}}$ is the band energy in cm⁻¹, $\tilde{\nu}_{1/2}$ is the bandwidth at half-height in cm⁻¹, ϵ is the molar absorptivity, and *r* in Å is taken as the distance between the interaction redox centers. Equation 1 can cover only a true Gaussian-shaped curve within a MV state in class II; two problems are conceivable: (1) The exact distance between interacting redox centers is experimentally obtained only for diabatic (interacting) redox centers. (2) Because the vibrational levels are higher than those assumed in class II, the IV-CT band shape collapses roughly from the form of the Gaussian band. There is the possibility of underestimating V because of these problems; however, we obtained V in this way in order to estimate the ET rate. When the electronic coupling is sufficiently strong, the thermal ET barrier ΔG^* and the thermal ET rate constant k_{th} were estimated using the following equations:¹⁰

$$\Delta G^* = \frac{\lambda}{4} - V + \frac{V^2}{\lambda} \tag{2}$$

$$k_{\rm th} = \nu_{\rm n} \exp(-\Delta G^*/RT) \tag{3}$$

where λ is the Marcus reorganization energy of the redox center obtained as $\tilde{\nu}_{max}$ and ν_n is the nuclear frequency factor, which includes both the solvent and conformation reorganization frequency required by charge transfer between the localized valence state. The theoretical maximum ET rate constant for an intramolecular ET can reach $10^{12}-10^{13}$ s⁻¹. We employ this ν_n of PDA derivatives in dichloromethane as 9×10^{12} s⁻¹ according to the previous literature by Lambert et al.¹² The k_{th} values of PDA⁺⁺, PDA-Me⁺⁺, PDA-Ph⁺⁺, PDA-Br⁺⁺, PDA-Th⁺⁺, PDA-'Bu⁺⁺, and BZ⁺⁺ are calculated to be 2.4×10^{11} , $1.1 \times$ 10¹¹, 7.6 × 10¹⁰, 1.3 × 10¹¹, 1.1 × 10¹¹, 3.9 × 10¹⁰, and 1.2 × 10¹¹ s⁻¹, respectively (Table 2). Nonsubstituted PDA showed the fastest ET. The ET rate decreases more efficiently with the introduction of bulky substituent such as methyl and *tert*-butyl due to the twisted orbitals on the N atoms rather than to the increase in the distance between the two redox centers. The electronic mixing coefficient α is an estimate of the electron delocalization: $\alpha = V/\tilde{\nu}_{max}$.^{8d,12b} A plot of α vs k_{th} , except for BZ, gave a straight line (Figure 4); this result supports the idea that the series of PDA derivatives have two local minima, and these are not the MV state in the class III state but the class II/III transition state.

Infrared Spectroelectrochemistry. In the case of PDA, the ν (N–H) stretching absorption attributed to the monocation radical was observed using IR-SEC^{21,22} in CH₂Cl₂/0.2 M TBAP (Figure 5a). The absorption around 3420 cm^{-1} assigned to the N-H stretching vibration in the neutral state decreases with the applied potential from 0 up to 0.5 V vs Ag/Ag⁺. On the other hand, a new absorption around 3247 cm^{-1} appeared. On applying a potential over 0.8 V vs Ag/Ag⁺, this absorption disappears. These results indicate that the absorption around 3247 cm⁻¹ is attributed to the N-H vibration of PDA in the monocation radical state. The intensity of the N-H vibration signal in the monocation radical state is larger than that in neutral state because the dipole moment of the N^{•+}-H moiety is larger than that of the N-H moiety. We ascertained the identification of the absorption of this N-H vibration in the monocation radical state around 3245 cm⁻¹ by potential sweeping from both directions on the oxidation side and on the reduction side. When electrochemically reducing N,N'-diphenyl-1,4-benzoquinonediimine (PDI), which is an oxidized form of PDA, in acetonitrile containing 0.2 M TBAP and 25 mM trifluoroacetic acid (TFA), a new absorption around 3245 cm⁻¹, attributed to the N-H vibration in the one-electron oxidized state, appeared at a potential from 0.4 to 0.2 V vs Ag/Ag⁺. On applying a potential under 0 V, the absorption disappears, and a new absorption around 3376 cm⁻¹ attributed to N-H stretching of the neutral state appears. The IR-SEC results of PDA and PDI under the same conditions are in accord; thus, the absorption around 3245 cm⁻¹ is determined to be the N–H vibrational stretching in the one-electron oxidized state. The adjacent weak signals (*) at the low-energy side of the genuine signals are thought to be the N-H vibration interacting with the supporting electrolyte, such as TBAP, because these signals are shifted to the lowenergy side by a more basic supporting electrolyte such as tetrabutylammonium tetrafluoroborate (TBABF₄). Similar results are obtained from the PDA-Br spectra (Figure 5b). The IR-SEC spectra were fitted by the Voigt function,¹⁵ and the Voigt profiles are collected in SI Tables 1 and 2. The shapes of these signals are fitted by the Voigt function as a convolution of Gaussian and Lorentzian function. These results indicate that each spectrum consisted of a single peak by the deconvolution of the spectrum the using the Voigt function because the difference in the N-H vibration energy between the line symmetry and the point symmetry of the molecular conformation is only about 2 cm⁻¹ based on the MO frequency calculation. In dichloromethane containing 0.2 M TBAP, the N-H vibrational stretching absorption maxima in the MV state of PDA++, PDA-Me++, PDA-Ph++, PDA-Br++, PDA-Th++, and BZ^{•+} are 3247, 3257, 3333, 3320, 3322, and 3253 cm⁻¹, respectively. All N-H vibrational spectra of the neutral and MV state are summarized in Table 3. The intensity of the N-H vibration signal in the monocation radical states is larger than in the neutral state because the dipole moment of the N^{•+}-H

TABLE 2: Band Shape Data for the IV-CT Band of PDA Derivatives in CH₂Cl₂ Containing 0.2 M TBAP at ca. 298 K

compd	$r^a/\text{\AA}$	$\nu_{\rm max}/{ m cm}^{-1}$	$v_{1/2}^{b}/cm^{-1}$	$\epsilon^{c}/\mathrm{M}^{-1}\mathrm{cm}^{-1}$	V^{d}/cm^{-1}	α^{e}	$\Delta G^{*f/}\mathrm{cm}^{-1}$	$k_{\rm th}^{g/s^{-1}}$
PDA* ⁺ PDA-Me* ⁺ PDA-Ph* ⁺ PDA-Br* ⁺ PDA-Th* ⁺ PDA-Tbu* ⁺ BZ* ⁺	5.56 5.56 5.56 5.56 5.56 5.56 5.54 9.89	$\begin{array}{c} 1.41 \times 10^{4} \\ 1.48 \times 10^{4} \\ 1.39 \times 10^{4} \\ 1.33 \times 10^{4} \\ 1.31 \times 10^{4} \\ 1.52 \times 10^{4} \\ 8.73 \times 10^{3} \end{array}$	$5.69 \times 10^{3} \\ 5.83 \times 10^{3} \\ 5.64 \times 10^{3} \\ 5.53 \times 10^{3} \\ 5.49 \times 10^{3} \\ 5.90 \times 10^{3} \\ 4.48 \times 10^{3} \\ \end{bmatrix}$	$\begin{array}{c} 1.37 \times 10^{4} \\ 1.18 \times 10^{4} \\ 9.81 \times 10^{3} \\ 1.07 \times 10^{4} \\ 9.51 \times 10^{3} \\ 8.90 \times 10^{3} \\ 1.87 \times 10^{4} \end{array}$	$\begin{array}{c} 3.78 \times 10^{3} \\ 3.72 \times 10^{3} \\ 3.23 \times 10^{3} \\ 3.23 \times 10^{3} \\ 3.10 \times 10^{3} \\ 3.44 \times 10^{3} \\ 1.57 \times 10^{3} \end{array}$	0.27 0.25 0.23 0.24 0.24 0.24 0.23 0.18	751 915 990 881 910 1130 896	$\begin{array}{c} 2.4 \times 10^{11} \\ 1.1 \times 10^{11} \\ 7.6 \times 10^{10} \\ 1.3 \times 10^{11} \\ 1.1 \times 10^{11} \\ 3.9 \times 10^{10} \\ 1.2 \times 10^{11} \end{array}$

^{*a*} The N–N distance from an UB3LYP/6-31G* optimization (the 3-21G* basis set was substituted for 6-31G* in the case of the bromine atom). ^{*b*} Observed bandwith at half-height. ^{*c*} For the highest absorption band given by $[M^+] = [M^+]_0 \sqrt{K_{co}}(2 + \sqrt{K_{co}})$, where $[M^+]_0 = [M]_0$ is the initial and final concentration of M and of M⁺, respectively. ^{*d*} $V = (0.0206/r)\sqrt{\tilde{\nu}_{max}\tilde{\nu}_{1/2}\epsilon}$. ^{*e*} $\alpha = V/\tilde{\nu}_{max}$. ^{*f*} $\Delta G^* = \lambda/4 - V + V^2/\lambda$. ^{*s*} $k_{th} = \nu_n \exp(-\Delta G^*/RT)$, $\nu_n = 9.0 \times 10^{12} \text{ s}^{-1}$, according to ref 12a.



Figure 3. IV-CT bands of PDA⁺⁺ (solid line) and PDA-Br⁺⁺ (dashed line) from spectroelectrochemical analysis in CH_2Cl_2 containing 0.2 M TBAP at ca. 298 K. Light path length: 1.0 mm; Gaussian band fits (dotted lines). Their potentials are 0.3 and 0.55 V (vs Ag/Ag⁺), respectively.



Figure 4. Correlation of electron-transfer rate $k_{\rm th}$ (s⁻¹) vs electronic mixing coefficient α for (\bullet) PDA derivatives and (\diamond) BZ.

moiety is larger than that of the N–H moiety. No N–H stretching spectra of two-electron-oxidized PDA derivatives in the dication state are detected in the area from 3500 to 3200 cm^{-1} .

Temperature Effect on v(N-H) and the Electron-Transfer Rate Constant. If the single peak which was obtained at room temperature in the IR spectra measurement was separately observed completely at low temperature due to coalescence, we can obtain the ET rate estimation using a Bloch-type equation on the IR spectra time scale as a second method. The variabletemperature IR spectra of the amines in PDA in the monocation radical state were determined from the temperature-controlled IR spectra in a quartz 1 mm cell (Figure 6a). The absorption band of PDA in the monocation radical state was observed at 298 K as a single peak due to the coalescence between the two kinds of N-H vibrational absorptions attributed to the neutral and monocation radical states. The single peak at 3247 cm^{-1} is gradually separated into two peaks at 3275 and 3243 cm⁻¹ on decreasing the temperature to 193 K. The absorption band analysis of PDA-Br in the monocation radical state gave the



Figure 5. ν (N–H) vibration spectra of several potentials of (a) PDA and (b) PDA-Br in CH₂Cl₂ containing 0.2 M TBAP at ca. 298 K. Light path length: 1.0 mm; Voigt function band fits (O). An Ag/Ag⁺ electrode is used as the reference. The marked peaks (*) are assigned to the ν (N–H) vibration interaction with the supporting electrolyte (TBAP) as minor peaks.

TABLE 3: Spectroelectrochemical Analysis of ν (N-H) Stretching Vibration

compd	ν (N-H) in the neutral state (cm ⁻¹)	ν (N-H) in the monocation radical state (cm ⁻¹)	$\Delta \nu$ (cm ⁻¹)
PDA	3420	3247	173
PDA-Me	3414	3257	157
PDA-Ph	3413	3333	80
PDA-Br	3401	3320	81
PDA-Th	3404	3322	82
BZ	3421	3253	168

ET rate by the same procedure and was observed at 298 K as a single peak at 3320 cm^{-1} and at 193 K as two peaks at $3342 \text{ and } 3315 \text{ cm}^{-1}$ (Figure 6b). No division of the peaks around 3420 cm^{-1} assigned to the N–H stretching vibration in PDA in the neutral state was observed in each temperature from 298



Figure 6. (a) ν (N–H) vibrational in the variable-temperature IR spectra of (a) PDA⁺⁺ and (c) PDA-Br⁺⁺. The recorded conditions are as follows: (a) in CH₂Cl₂ solution containing 0.2 M TBAP at 193/203/213/233/253/273/298 K; (c) in CD₂Cl₂ solution containing 0.2 M TBAP at 193/213/233/253/273/298 K. Relative simulated deconvolution spectra using the Bloch-type equation as a function of the intramolecular ET rate constant (k_{el}) of (b) PDA⁺⁺ and (d) PDA-Br⁺⁺.

to 193 K (SI Figure 1). The simulated line widths are narrower than the observed ones because the simulated ones consist of the Lorentzian functions based on the well-established methods of dynamic NMR spectroscopy,¹⁶ but observed ones are obtained as the Voigt functions, which are broader than the simple Lorentzian functions due to the IR absorptions in liquid-phase systems.

Some reasons why the peak could separate clearly into two in this way are considered. (1) The gap in the vibration spectra $(\Delta \nu)$ between N–H and N^{•+}–H is sufficiently widely separated to be observed. (2) The electron coupling is weak so that the compounds have two local minima in the valence trapped or the charge localized state, and the electron-transfer rate is slower than the IR time scale at low temperature due to electron trapping at the amine site. The ET rate at room temperature (298 K) is calculated as follows. Each IR spectrum was analyzed by curve fitting to the Voigt Function shown in SI Figures 2 and 3. The information on the peak position and width was used for the analysis. We estimated the ET rate at room temperature by extrapolation of the Eyring plot using the activation free

 TABLE 4: Selected Geometrical Parameters in the Monocation Radical State

	dihedral angle (deg) ^a			
$compd^b$	$C_1C_2N_3C_4{}^c$	$C_2N_3C_4C_5{}^d$	$C_6C_2N_3H_7$	
PDA•+	13.2	36.2	12.9	
PDA-Me•+	13.0	39.1	13.8	
PDA-Ph ^{•+}	14.3	37.2	11.3	
PDA-Th•+	16.7	37.2	14.4	
PDA- ^t Bu ^{•+}	17.1	40.4	16.5	
BZ•+	12.3	37.0	12.0	
2,6-DMPDA++	5.8	64.7	11.1	
PDA	32.7 (29.9) ^e	18.9 (23.9) ^e	25.8	
2,6-DMPDA	2.3 (9.1) ^f	70.8 (70.1) ^f	38.2	

^{*a*} Computed at the DFT UB3LYP/6-31G* level. ^{*b*} Atomic labels are shown in Chart 1. ^{*c*} The inside C_2 – N_3 bond. ^{*d*} The outside N_3 – C_4 bond. ^{*e*} From the X-ray structural analysis in ref 6c. ^{*f*} From the X-ray structural analysis.

energy (ΔG^{\ddagger}) with which a Bloch-type equation plot and the temperature-dependent IR spectra most agree. The ΔG^{\ddagger} of PDA and PDA-Br were determined to be 420 and 522 cm⁻¹, respectively (SI Figure 4). The k_{et} values between the N–H neutral and N^{•+}–H at room temperature of PDA^{•+} and PDA-Br^{•+} were estimated to be 8.2×10^{11} and 5.0×10^{11} s⁻¹ (Figure 6), which are in good agreement with the order from the IV-CT band analysis using the Marcus–Hush theory.

The results for ET from the Marcus—Hush theory (k_{th}) are smaller than that from the Bloch-type equation analysis (k_{et}) due to the overestimation of the distance between redox centers (r) or the underestimation of the nuclear frequency factor (ν_n). By making typical assumptions, we estimated the r' from the k_{EX} using Marcus—Hush theory ($\nu_n = 9.0 \times 10^{12} \text{ s}^{-1}$),^{12a} and the r' value for PDA⁺⁺ and PDA-Br⁺⁺ are 4.79 (5.56) and 4.70 (5.56) Å (calculated), respectively. These results show a reasonable underestimate of the electron coupling constant (V) in the class II/III transition state by a factor of the 0.85–0.86.

Electronic Structure Calculations. Reasonable molecular structure estimations for the PDA derivatives in the neutral and MV states were provided by the UB3LYP/6-31G* level using the Gaussian98 package.^{23–25} Because we are interested in the location of the point symmetric geometry configuration (as a reference configuration),¹⁴ the optimization of the monocation radical states has been carried out with symmetry constraints. The selected geometric parameters are summarized in Table 4. The linear correlation between the experimental value of ΔE in Table 1 and the dihedral angle of the C₂-N₃ bond inside in the monocation radical state was found because the ΔE indicates the magnitude of the interaction between the redox sites. To increase the electronic coupling, the HOMO orbital, which participates in the electron transfer, should be concentrated on the phenyl ring at the center. The introduction of a nonconjugated bulky group, such as methyl or tert-butyl, to the center phenyl ring causes the whole molecular structure to be out-ofplane due to the twist of the inside C_2-N_3 bond. As a result, the electric interaction between N atoms through the π -bond becomes weak. The introduction of a π -conjugated group such as phenyl or thienyl, which are expected to function as an electron-donating group, does not result in an increase with the HOMO orbital level on the phenyl ring at the center but also twists the whole molecule. Because the electron densities of the phenyl ring at the center decline mainly due to twisting of the inside C₂-N₃ bond by the steric hindrance of a substituent in the phenylene ring, the ET rate thus decreases.

In the case of PDA, which showed the fastest ET rate, the inside C_2 -N₃ bond is hardly twisted and the lobe of *n* electrons on the N atoms are aligned in line in the same plane across the



Figure 7. Contour plots of the HOMO α molecular orbitals of (a) PDA⁺⁺ and (b) 2,6-DMPDA⁺⁺ as obtained at the B3LYP/6-31G* level. ORTEP diagrams of (c) 2,6-DMPDA in the neutral state.

phenyl at the center, so that the interaction of the orbital is strong. However, the HOMO orbital is seen to intrude into the outer phenyl rings (Figure 7a).

On the basis of these results, we designed 2,6-DMPDA which is substituted in the outside phenyl ring. In the case of N,N'bis(2,6-dimethylphenyl)-1,4-phenylenediamine (2,6-DMPDA), because the twist of the outside N₃-C₄ bond is large, due to steric hindrance, the *n* electrons at the HOMO orbital intruding into the outer phenyl are suppressed, and the interaction with the outside phenyl is small. On the other hand, because the twist of the inside C₂-N₃ bond is small, the *n* electrons on the N atoms are aligned approximately in the same plane with the phenyl ring at the center, and the concentration of the HOMO orbital on the phenyl ring at the center occurs so that the electronic interaction increases. There is little intrusion of the HOMO orbitals outside of the phenyl compared with PDA, and the electronic coupling between amines is expected to increase more than in PDA.

We compared the structures between 2,6-DMPDA and PDA in the monocation radical state from the viewpoint of "the twist of the N orbitals" as two dihedral angles of inner and outer C–N bonds. The twist of the inside C₂–N₃ bond of 2,6-DMPDA^{•+} is smaller than that of PDA^{•+} (Table 4). Moreover, the dihedral angles of the outer phenyl and N in PDA^{•+} and 2,6-DMPDA^{•+} are 36.2° and 64.7°, respectively (Figure 7a,b) and so prevent the intrusion of the electrons of the N atom into the outer phenyl. These results support the fact that it is easy to localize the HOMO orbital on the phenyl ring at the center. The X-ray structural analysis in the neutral state (Figure 7c) and electronic structure calculations also support these results. The *n* electrons on the N atom overlap the π electrons of the inner phenyl ring on the same plane, whose structure prevented intrusion of the HOMO orbital into the outer *N*-phenyl ring due



Figure 8. IV-CT bands of PDA⁺⁺ with 0.5 M TFA (solid line) and 2,6-DMPDA⁺⁺ with 0.63 M TFA (dashed line) from spectroelectrochemical analysis in acetonitrile containing 0.2 M TBABF₄ at ca. 298 K. Light path length: 1.0 mm; Gaussian band fits (dotted lines). Fitting for 2,6-DMPDA⁺⁺ in high-energy side is impossible. Their potentials are 0.30 V (vs Ag/Ag⁺).

to twisting of the outer C-N bond by steric hindrance. Comparing the HOMO orbital of PDA with that of 2,6-DMPDA, the HOMO electron density of 2,6-DMPDA is higher than that of PDA (Figure 7a,b).

Electrochemistry and the UV-vis SEC of Outer Phenyl-Modified PDA Derivatives. The introduction of a substitutent into the central phenylene ring of PDA resulted in decreases in the electron density on the amine atoms due to twisting of the inner C-N bond of the homo orbital, in which the ET between the two amines is suppressed. The cyclic voltammograms of 2,6-DMPDA showed two reversible redox processes in acetonitrile containing 0.2 M tetrabutylammonium tetrafluoroborate (TBABF₄) and 0.63 M trifluoroacetic acid (TFA).²⁶ The E°_{1} , E°_{2} , and ΔE of PDA with 0.5 M TFA are 0.20 V, 0.48 V (vs Ag/Ag⁺), and 0.28 V, respectively (SI Figure 5). The ΔE of 2,6-DMPDA, which is an ortho-dimethyl-substituted PDA, is drastically increased. This result shows that the interaction between redox sites is increased. The ΔE of 2,6-DMPDA in the CV was larger than that of PDA. This result suggests a higher interaction in 2,6-DMPDA between the two amines than that in PDA, which shows the fastest ET rate among the PDA derivatives.

Under the same CV conditions, the IV-CT band of 2,6-DMPDA^{•+} in the MV state increased around 555 nm (18 000 cm^{-1}) from a potential of 0.05 to 0.3 V vs Ag/Ag⁺ from the UV-vis SEC in acetonitrile (Figure 8). The $\nu_{\rm max}$ of PDA⁺ is at 698 nm (Figure 8). The high-energy side of the absorption spectrum after one-electron oxidation did not fully agree with the Gaussian curve for 2,6-DMPDA⁺⁺ because the large electron coupling (when $2V > \lambda$) pushes up a cutoff to the high-energy side of the Gaussian curve.^{2c} The electron coupling V, the thermal ET barrier ΔG^* , and the thermal ET rate constant k_{th} were estimated using the Marcus-Hush theory by analysis of the absorption wave shapes. The $k_{\rm th}$ of PDA^{•+} in acetonitrile was $3.1 \times 10^{11} \text{ s}^{-1.27}$ On the other hand, the mechanically calculated $k_{\rm th}$ of 2,6-DMPDA^{•+} was $4.0 \times 10^9 \, {\rm s}^{-1.27}$ This result suggests that the 2,6-DMPDA^{•+} is in class III, and so the Marcus-Hush theory does not apply.

Solvent Effect. The wavelength of the absorption maximum ν_{max} of the IV-CT band for 2,6-DMPDA⁺⁺ is independent of the solvents. The correlation of ν_{max} and $(1/n^2 - 1/D)^{8c,28}$ for PDA⁺⁺ has a slope, but the ν_{max} of 2,6-DMPDA does not obey the equation $\lambda = (q^2/8\pi D_0)(1/a)(1/n^2 - 1/D)$ from the Marcus theory due to the electron delocalization in a class III state (Figure 9). This means that the absorption maximum based on the optical diabatic path as the ET path is greater than the Marcus reorganization. The coalescence analysis of 2,6-DMPDA



Figure 9. Solvent effect of (\bigcirc) 2,6-DMPDA⁺⁺ and (\square) PDA⁺⁺ for IV-CT band ν_{max} recorded in PhCl, CHCl₃, CH₂Cl₂, DMSO, DMF, and MeCN.

in the temperature-dependent IR spectra measurement for a Bloch-type equation analysis was unfortunately not observed because complete delocalization of the monocation radical occurred.

Conclusion

The electron-transfer rates of PDA derivatives in the MV state were investigated using two methods: the Marcus—Hush theory and a Bloch-type equation analysis. These results are in good agreement with each other. The electronic coupling intensity between the two amines is fixed by the twist of n electrons on the N atoms based on the substituent effect. We first demonstrated the PDA derivatives of IV-CT in classes II and III by the introduction of a substituent into the inner or outer phenyl rings.

Experimental Section

General. NMR spectra were recorded on a JEOL JMN400 FT-NMR spectrometer (400 MHz) in DMSO- d_6 , CD₃CN, CDCl₃ or THF- d_8 + TMS internal standard) solution. MALDI–TOF-mass spectra were obtained on a Shimadzu/Kratos KO-MPACT MALDI mass spectrometer (positive mode; matrix: dithranol). The infrared spectrum was obtained with a potassium bromide pellet using a JASCO FT-IR-460Plus.

Materials. *N,N'*-Diphenyl-1,4-phenylenediamine (PDA) was purchased from Aldrich Chemical Co., Inc. 2,5-Dimethyl-1,4benzoquinone and 2,5-di-*tert*-butyl-1,4-benzoquinone were from Tokyo Kasei Co., Ltd. *N,N'*-Diphenylbenzidine (BZ) and all other chemicals were purchased from Kantoh Kagaku Co. The following compounds were prepared according to literature procedures: 2,5-dibromo-*N,N'*-diphenyl-1,4-phenylenediamine (PDA-Br),¹⁸ 2,5-diphenyl-*N,N'*-diphenyl-1,4-phenylenediamine (PDA-Ph),¹⁸ *N,N'*-diphenyl-2,5-di-thiophen-2-yl-1,4-phenylenediamine (PDA-Th).¹⁸

Syntheses. Synthesis of 2,5-Dimethyl-N,N'-diphenyl-1,4-phenylenediamine (PDA-Me). Aniline (9.48 g, 102 mmol) was dissolved in chlorobenzene (40 mL) under nitrogen, and titanium(IV) tetrachloride (3.66 g, 19.3 mmol) was added dropwise at 90 °C. The addition funnel was then rinsed with chlorobenzene (20 mL). 2,5-Dimethyl-1,4-benzoquinone (1.00 g, 7.3 mmol) dissolved in chlorobenzene (100 mL) was added dropwise over 15 min to the mixture. The mixture was stirred in an oil bath at 125 °C for 12 h. The precipitate was removed by filtration and washed with chlorobenzene (20 mL). The filtrate was concentrated, and the compound PDA-Me (0.99 g, 47%, white powder) was isolated by silica gel chromatography (hexane:dichloromethane = 1:1). PDA-Me: ¹H NMR (400 MHz, DMSO-d₆, TMS standard, ppm) δ : 7.27 (s, 2H), 7.12 (dd, J = 7.3, 7.8 Hz, 4 H), 7.00 (s, 2H), 6.75 (d, J = 7.8 Hz, 4H), 6.66 (t, J = 7.3 Hz, 2H), 2.09 (s, 6H). ¹³C NMR (100 MHz, DMSO- d_6 , TMS standard, ppm) δ : 146.1, 135.9, 129.1, 128.9, 124.3, 117.6, 114.6, 17.7. IR (KBr, cm⁻¹): 3396 (N–H). MALDI–TOF-mass calcd: 288.4 [M⁺]. Found: 287.2. Anal. Calcd for C₂₀H₂₀N₂: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.33; H, 6.87; N, 9.74.

Synthesis of 2,5-Di-tert-butyl-N,N'-diphenyl-1,4-phenylenediamine (PDA-'Bu). Aniline (9.48 g, 102 mmol) was dissolved in chlorobenzene (40 mL) under nitrogen, and titanium(IV) tetrachloride (3.40 g, 17.9 mmol) was added dropwise at 90 °C. The addition funnel was then rinsed with chlorobenzene (20 mL). 2,5-Dimethyl-1,4-benzoquinone (1.5 g, 6.81 mmol) dissolved in chlorobenzene (100 mL) was added dropwise over 15 min to the mixture. The mixture was stirred in an oil bath at 125 °C for 12 h. The precipitate was removed by filtration and washed with chlorobenzene (20 mL). The filtrate was concentrated, and the compound PDA-'Bu (0.406 g, 16%, white powder) was isolated by silica gel chromatography (hexane: dichloromethane = 2:1). PDA- 'Bu: ¹H NMR (400 MHz, CD₃CN, TMS standard, ppm) δ : 7.24 (s, 2H), 7.16 (dd, J =7.8, 7.8 Hz, 4 H), 6.72-6.69 (m, 6H), 5.82 (s, 2H), 1.30 (s, 18H). ¹³C NMR (100 MHz, CD₃CN, TMS standard, ppm) δ : 148.5, 145.0, 138.1, 130.0, 128.2, 118.7, 115.3, 35.2, 30.8. IR (KBr, cm⁻¹): 3389 (N-H). MALDI-TOF-mass calcd: 372.6 [M⁺]. Found: 370.9. Anal. Calcd for C₂₆H₃₂N₂: C, 83.82; H, 8.66; N, 7.52. Found: C, 83.70; H, 8.59; N, 7.51.

Synthesis of N,N'-Bis(2,6-dimethylphenyl)-1,4-phenylenediamine (2,6-DMPDA) via N,N'-Bis(2,6-dimethylphenyl)-1,4benzoquinonediimine. 2,6-Dimethylaniline (0.73 g, 6.0 mmol) and triethylamine (1.21 g, 12.0 mmol) were dissolved in chlorobenzene (15 mL) under argon, and titanium(IV) tetrachloride (0.85 g, 4.5 mmol) was added dropwise at 60 °C. The addition funnel was then rinsed with chlorobenzene (1 mL). 1,4-Benzoquinone (0.34 g, 3.0 mmol) dissolved in chlorobenzene (7 mL) was added dropwise over 15 min to the mixture. The mixture was stirred in an oil bath at 60 °C for 2 h. The precipitate was removed by filtration and washed with chlorobenzene (5 mL). The filtrate was concentrated, and the compound N,N'-bis(2,6-dimethylphenyl)-1,4-benzoquinonediimine (0.69 g, 74%, orange powder) was isolated by silica gel chromatography (CHCl₃). N.N'-Bis(2,6-dimethylphenyl)-1,4benzoquinonediimine: ¹H NMR (400 MHz, CDCl₃, TMS standard, ppm) as mixture of two syn-anti isomers, δ : 7.20 (m, 1H), 7.08-6.91 (m, 7H), 6.48 (dd, J = 2.4, 10.3 Hz, 1H), 6.23 (m, 1H), 2.01 (s, 7H), 1.97 (s, 5H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, ppm) as mixture of two syn-anti isomers, δ : 158.9, 158.8, 148.0, 147.9, 136.7, 135.9, 127.8, 127.7, 125.7, 124.7, 124.5, 124.0, 123.9, 18.2. MALDI-TOFmass calcd: 315.4 [M + 1⁺]. Found: 315.1.

N,*N*'-Bis(2,6-dimethylphenyl)-1,4-benzoquinonediimine (0.314 g, 1.00 mmol) was dissolved in acetonitrile (30 mL) under nitrogen, and tin(II) dichloride (1.21 g, 15 mmol) and trifluoroacetic acid (1.7 g, 15 mmol) were added. The mixture was stirred for 13.5 h at room temperature, and triethylamine (1.5 g, 15 mmol) was added. The filtrate was concentrated, and the compound 2,6-DMPDA (0.307 g, 97%, white powder) was isolated by silica gel chromatography (hexane:THF = 2:1). 2,6-DMPDA: ¹H NMR (400 MHz, THF-*d*₈, TMS standard, ppm) δ : 8.81 (d, *J* = 7.3 Hz, 4H), 8.70 (t, *J* = 7.3 Hz, 2H), 8.11 (s, 4H), 7.79 (s, 2H), 3.95 (s, 12H). ¹³C NMR (100 MHz, THF-*d*₈, TMS standard, ppm) δ : 140.3, 139.0, 134.5, 128.1, 124.0, 114.9, 17.8. IR (KBr, cm⁻¹): 3396 (N–H). MALDI–TOF-mass calcd: 316.4 [M⁺]. Found: 316.2. Anal. Calcd for C₂₂H₂₄N₂: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.32; H, 7.67; N, 8.70.

Electrochemical Measurements. Electrochemical analyses were performed using an electrochemical workstation (BAS Co., Ltd., model ALS-660) under the following conditions. Cyclic voltammetry (CV) was carried out under a N₂ atmosphere. A glassy carbon (GC) disk electrode (0.071 cm²) was used as the working electrode and was polished with 0.3 μ m alumina before the experiments. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/Ag⁺ one, which was placed in the main cell compartment. The formal potential of the ferrocene/ferrocenium couple was 0.076 V vs this reference electrode in acetonitrile. All potentials are quoted with respect to this Ag/Ag^+ reference electrode. The potential was normalized to the ferrocene/ferrocenium couple in acetonitrile. The scanning rate was 100 mV/s. In all cases, a 0.2 M solution of tetrabutylammonium perchlorate (TBAP) in dichloromethane was used. These PDA derivatives underwent a twostep oxidation from the amine to the monocation radical to the imine forms. In the case of using 0.2 M solution of TBABF₄ in acetonitrile without trifluoroacetric acid (TFA), the second redox couple was not reversible because the oxidative half-reaction of the second couple involves the loss of one electron and two protons, while the cathodic half-reaction entails the gain of one electron and two protons. However, in dichloromethane with 0.2 M TBAP, the two reversible redox couples were confirmed without proton transfer because the solvent donor number of dichloromethane is lower than that of acetonitrile.

IV-CT Spectra Measurement. Controlled-potential absorption spectra were obtained with an optically transparent thinlayer electrode quartz cell (light path length = 1 mm). The working and the counter electrodes were platinum mesh and a platinum coil, respectively. The potential was applied with a Hokuto-Denko potentio/galvanostat, model HA-501G, and referred to Ag/Ag⁺. The spectra were measured with a Shimadzu UV-3150PC spectrophotometer. All spectroelectrochemical measurements were carried out at ca. 298 K under a nitrogen atmosphere.

IR-Spectroelectrochemistry. Controlled-potential absorption spectra of ν (N–H) vibration spectra were obtaind using the same electrochemical apparatus as in the IV-CT spectra measurement. The spectra were measured with a JASCO FT-IR-460Plus.

Variable-Temperature IR Spectra of the Amines in the Mixed-Valence State. Controlled-temperature absorption spectra were obtained with 1 mM PDA*+/PDA-Br*+ in CH₂Cl₂/CD₂-Cl₂ with 0.2 M TBAP prepared by electrochemical one-electron oxidation in a quartz cuvette (light path length = 1 mm). The variable temperature was supplied by an OXFORD cryostat, model Optistat DN. The spectra were measured with a JASCO FT-IR-460Plus.

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Supporting Information Available: Fitting procedures and parameters for spectroelectrochemical analysis, CIF file, electrochemical analysis, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Because of the strong interaction between the redox centers, the second oxidation of 2,6-DMPDA in dichloromethane without TFA is not reversible accompanied by the proton removal due to higher potential around 0.7 V (vs Ag/Ag⁺). The addition of TFA restrains the proton removal, and the reversible redox couples are observed.

(27) $\nu_n = 1.35 \times 10^{13} \text{ s}^{-1}$ as an appropriate value in acetonitrile according to ref 12b.

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