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Estimate of the Stabilization Energy of Cation Radicals Formed in Poly(*N*-vinylcarbazole) and Its Dimer Model Compounds by an Ion Radical Transfer Method

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ABSTRACT: The stabilization energies of the carbazole cation radicals were estimated by the ion radical transfer method. The carbazole cation radicals ($Cz^{\bullet+}$) were formed photochemically in poly(*N*-vinylcarbazole) (PVCz) and its dimer model compounds, and they were stabilized by the interaction with neighboring carbazole (Cz) chromophores. Due to the stabilization, the Cz cation radical in PVCz is not transferred to a cation radical acceptor, 4-(dimethylamino)styrene (DMASt), which has a lower oxidation potential than the Cz chromophore, whereas the cation radical of monomeric *N*-ethylcarbazole is transferred to DMASt easily. The stabilization energies of $Cz^{\bullet+}$ were evaluated from the rate constants of cation radical transfer to DMASt. Measurements were made on PVCz, its oligomer (DP = 7–8), the copolymer with styrene, and the monomer and dimer model compounds. The stabilization energies for the dimer model compounds were estimated to be 0.3–0.4 eV (7–9 kcal/mol) for the sandwich dimer cation radical and ca. 0.1 eV (2 kcal/mol) for the second dimer cation radical, and the Cz cation radical in PVCz is most stabilized among the compounds. In the case of PVCz, there are considered to be some polymer effects such as steric hindrance besides the stabilization due to the neighboring interaction.

Introduction

Recently the photophysical and photochemical processes of polymers having aromatic chromophores as pendant groups have been extensively studied.[1–4] Such polymers show several photophysical and photochemical properties characteristic of a high local concentration of chromophores, e.g., highly efficient intramolecular excimer formation and energy migration in polymers[5–8] and a specific solvent effect and the stabilization of ion radical of chromophores.[9,10]

As for the chromophore interaction in polymer systems, excimer formation in poly(*N*-vinylcarbazole) (PVCz) has been extensively studied.[11–14] The isotactic diad in PVCz forms the sandwich excimer with the emission band around 420 nm similarly to its dimer model compound, *meso*-2,4-di-*N*-carbazolylpentane[15,16] (*m*-DCzPe), whereas the syndiotactic diad in PVCz forms the second excimer with the emission band around 370 nm similarly to its dimer model compound, *rac*-2,4-di-*N*-carbazolylpentane[15,16] (*r*-DCzPe). In the case of the cation radicals, a change of the transient absorption spectra corresponding to the excimer conformations has been observed.[17] Namely, 1,3-di-*N*-carbazolylpropane (DCzPr) and *m*-DCzPe form the sandwich dimer cation radicals[18] with a completely overlapping conformation and their absorption bands appear around 760 and 770 nm, respectively, whereas *r*-DCzPe forms the second dimer cation radical with a partially overlapping conformation and has a broad absorption band around 710 nm. The cation radical $Cz^{\bullet+}$ in PVCz has a broad absorption band around 750 nm,[19,20] and it is stabilized much more than the *N*-ethylcarbazole (EtCz) cation radical.[21] To investigate the electronic properties of cation radicals, ESR,[22] CIDNP,[23] and charge-resonance band measurement[24] have been used.

In this study, the stabilization energies of the cation radicals for the dimer model compounds are estimated quantitatively by the cation radical transfer method. These stabilization energies are discussed in connection with the conformations of two Cz chromophores. The stabilization energy of $Cz^{\bullet+}$ in PVCz is discussed compared with the cases of the oligomer (OVCz) and poly[(*N*-vinylcarbazole)-*co*-styrene] (P(VCz–St)).

Experimental Section

A. Cation Radical Transfer Method.[25] When an electron donor (D_1) is photoexcited in the presence of a sufficient concentration of an electron acceptor (A) in a polar solvent, an electron transfer from an excited singlet donor (D_1^*) to A produces a cation radical ($D_1^{\bullet+}$) and an anion radical ($A^{\bullet-}$). This process is much faster than the succeeding processes. If the second electron donor (D_2, cation radical acceptor), which is a stronger electron donor than D_1, is added to this system, cation radical transfer from $D_1^{\bullet+}$ to D_2 (an electron transfer from D_2 to $D_1^{\bullet+}$) occurs (eq 1) and this process can be observed directly by the transient absorption of $D_1^{\bullet+}$ and $D_2^{\bullet+}$. This process competes with the recombination of $D_1^{\bullet+}$ with $A^{\bullet-}$ (eq 2), but it is possible to make this cation radical transfer the main process by adjusting the concentration of D_2 properly. $D_2^{\bullet+}$ produced by the cation radical transfer also decays by recombination with $A^{\bullet-}$ (eq 3). The processes, eq 1–3, lead to the following rate equations

$$D_1^{\bullet+} + D_2 \xrightarrow{k_{tr}} D_1 + D_2^{\bullet+} \tag{1}$$

$$D_1^{\bullet+} + A^{\bullet-} \xrightarrow{k_{r1}} D_1 + A \tag{2}$$

$$D_2^{\bullet+} + A^{\bullet-} \xrightarrow{k_{r2}} D_2 + A \tag{3}$$

$$d[D_1^{\bullet+}]/dt = -k_{tr}[D_1^{\bullet+}][D_2] - k_{r1}[D_1^{\bullet+}][A^{\bullet-}] \tag{4}$$

$$d[D_2^{\bullet+}]/dt = k_{tr}[D_1^{\bullet+}][D_2] - k_{r2}[D_2^{\bullet+}][A^{\bullet-}] \tag{5}$$

$$d[A^{\bullet-}]/dt = -k_{r1}[D_1^{\bullet+}][A^{\bullet-}] - k_{r2}[D_2^{\bullet+}][A^{\bullet-}] \tag{6}$$

where k_{tr} is the rate constant of the cation radical transfer, and k_{r1} and k_{r2} are the rate constants of the recombination of $D_1^{\bullet+}$ with $A^{\bullet-}$ and of $D_2^{\bullet+}$ with $A^{\bullet-}$, respectively. Hence if the transient decay for $D_1^{\bullet+}$, $D_2^{\bullet+}$, and $A^{\bullet-}$ is measured by the laser photolysis method and simulated by eq 4–6, the rate constant k_{tr} is determined.

In a simple case, k_{tr} can be estimated by the transient absorption decay at the peak wavelength of $D_1^{\bullet+}$: if the rate of the cation radical transfer from $D_1^{\bullet+}$ to D_2 is much faster than that of the recombination of $D_1^{\bullet+}$ with $A^{\bullet-}$ ($k_{tr}[D_2] \gg k_{r1}[A^{\bullet-}]$), eq 4 can be solved to give eq 7 by neglecting the second term, where

$$\ln [OD(D_1^{\bullet+})] = k_{tr}[D_2]t + C \tag{7}$$

C is a constant. Consequently, k_{tr} can be determined by the slope of the ln [OD($D_1^{\bullet+}$)] versus time plot.

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Table I
Rate Constants and Free Energy Change of a Cation Radical Transfer in EtCz–D_2–A Systems

no.	$[D_2]/10^{-4}$ M	$[A]/10^{-2}$ M	$k_{tr}/10^9$ M^{-1} s^{-1}	$\Delta G°$/eV
1	TMPD, 2.5	DCNB, 2.0	13.1	−1.04
2	DMASt, 2.8	DMTP, 1.0	11.0	−0.54
3	DMT, 3.6	DCNB, 1.9	8.9	−0.46
4	DMA, 4.0	DCNB, 1.9	9.7	−0.41
5	DPA, 2.0	DMTP, 2.0	7.8	−0.23
6	TPA, 2.5	DMTP, 2.0	7.8	−0.19
7	DMI, 4.0	DMTP, 2.0	6.6	−0.12

To measure the rate constants of the cation radical transfer satisfactorily, a set of D_1–D_2–A systems must satisfy the following conditions. First, D_1 is photoexcited selectively by a laser pulse, and the electron transfer from D_1* to A is sufficiently fast. Second, the transient absorption bands of $D_1^{\bullet+}$, $D_2^{\bullet+}$, and $A^{\bullet-}$ are separated enough to be analyzed. The sets of the D_1–D_2–A system measured in this study satisfy these requirements.

B. Chemicals. 1. Electron Donors (D_1). *N*-Ethylcarbazole (EtCz, Aldrich Chemical Co.) was purified by recrystallization. 1,3-Di-*N*-carbazolylpropane (DCzPr) was prepared from 1,3-dibromopropane (Wako Pure Chemical Industry, Ltd.) and sodium carbazole[26] and was purified by recrystallization from a mixture of dichloromethane and hexane. *rac*- And *meso*-2,4-di-*N*-carbazolylpentane (*r*- and *m*-DCzPe) were synthesized from 2,4-bis(tosyloxy)pentane,[15] which was prepared from 2,4-pentanediol (Tokyo Kasei Kogyo Co., Ltd.).[27] The racemic and meso isomers of DCzPe were separated by silica gel column chromatography and by liquid chromatography (Japan Spectroscopic Co., Ltd.) with the eluent of a mixture of hexane and ethyl acetate (7:1) and were purified by recrystallization from ethanol. Poly(*N*-vinylcarbazole) (PVCz, Tokyo Kasei Kogyo Co., Ltd., $M_w > 1 \times 10^5$) was purified by precipitation from a benzene solution into methanol several times. Poly[(*N*-vinylcarbazole)-*co*-styrene], abbreviated as P(VCz–St), was prepared by radical copolymerization using an AIBN initiator in degassed benzene at 60 °C. The molecular weight determined by GPC (Toyo Soda HLC 802 UR) with a GMH6 column was $M_w \simeq 7 \times 10^4$. The fraction of Cz units in the copolymer was determined to be ca. 10 mol % by elemental analysis. The oligomer (OVCz) of VCz was prepared by radical polymerization initiated by AIBN in toluene and fractionated by GPC (Toyo Soda HLC 802 R) with a G2000HG column. The fraction of DP = 7 and 8 which is denoted as OVCz was used for the measurements.

2. Electron Acceptors (A). Dimethyl terephthalate (DMTP, Wako Pure Chem. Ind., Ltd.) and 1,2-dicyanobenzene (DCNB, Tokyo Kasei Kogyo Co., Ltd.) were purified several times by recrystallization.

3. Cation Radical Acceptors (D_2). Similar amine compounds were used as the cation radical acceptor. 4-(Dimethylamino)styrene (DMASt) was prepared from 4-(dimethylamino)benzaldehyde (Nakarai Chemicals, Ltd.)[28] and purified by distillation under reduced pressure. *N*,*N*-Dimethyl-1,4-toluidine (DMT, Wako Pure Chemical Industry, Ltd.) and *N*,*N*-dimethylaniline (DMA, Wako Pure Chem. Ind., Ltd.) were purified by distillation under reduced pressure. *N*,*N*,*N′*,*N′*-Tetramethyl-1,4-phenylenediamine (TMPD, Tokyo Kasei Kogyo Co., Ltd.), diphenylamine (DPA, Tokyo Kasei Kogyo Co., Ltd.), triphenylamine (TPA, Tokyo Kasei Kogyo Co., Ltd.), and 1,2-dimethylindole (DMI, Aldrich Chemical Co.) were purified by recrystallization.

4. Solvents. Acetonitrile (MeCN, Wako Pure Chemical Industry, Ltd.) was refluxed over P_2O_5 several times and was fractionally distilled. Spectroscopic grade of *N*,*N*-dimethylformamide (DMF, Dotite Spectrosol) was used without further purification.

C. Transient Absorption Measurements. The transient absorption spectra of the ion radicals and the decays were measured by nanosecond laser photolysis. The carbazole chromophore was selectively photoexcited by the second harmonic pulse (347 nm, pulse energy 10 mJ, fwhm 14 ns) of a Q-switched giant pulse ruby laser (NEC SLG2009). The details of the laser photolysis apparatus have been described elsewhere.[25] All samples for laser photolysis were degassed by the freeze–pump–thaw method in a 1-cm quartz cell. The DMF solvent was used for PVCz, OVCz, and P(VCz–St), and the MeCN solvent was used for other systems. MeCN solvent is preferable since the oxidation potentials are also measured in MeCN, but DMF was used for its good solubilizing power of the polymers. As for the concentration of electron donors, the optical density at 347 nm was adjusted to about unity. The cation radical transfer from $D_1^{\bullet+}$ to D_2 was measured at the concentrations shown in Tables I and II. The rate constants of the recombination (k_{r1}, k_{r2}) and the molar extinction coefficients of individual ion radicals were determined by the laser photolysis for two-component systems (D_1–A and D_2–A systems). The transient absorption spectra of cation radicals, $TMPD^{\bullet+}$, $DMASt^{\bullet+}$, $DMT^{\bullet+}$, $DMA^{\bullet+}$, $DPA^{\bullet+}$, and $TPA^{\bullet+}$, have the absorption peaks at 620, 640, 470, 680, 670, and 670 nm, respectively. The transient absorption spectrum of $DMI^{\bullet+}$ could not be detected by the present nanosecond laser photolysis. This may be due to the small molar extinction coefficient of $DMI^{\bullet+}$. However, DMI under γ-ray irradiation in the rigid matrix of *sec*-butyl chloride at 77 K gives an absorption band around 540–600 nm, which is ascribed to $DMI^{\bullet+}$. The absorption peaks of $DMTP^{\bullet-}$ and $DCNB^{\bullet-}$ appear at 530 and 375 nm, respectively. The absorption spectra of these cation radicals and anion radicals were confirmed by γ-ray irradiation in rigid matrices of *sec*-butyl chloride and of 2-methyltetrahydrofuran at 77 K, respectively.[29]

Table II
Rate Constants of Cation Radical Transfer in D_1–DMASt–DMTP Systems

no.[a]	$[D_1]$	$[D_2]^b/10^{-4}$ M	$[A]^b/10^{-2}$ M	$k_{tr}/10^9$ M^{-1} s^{-1}
8[c]	EtCz	2.8	1.0	11.0
9	*r*-DCzPe	2.8	1.0	9.8
10	*m*-DCzPe	2.8	1.0	8.2
11	DCzPr	3.3	2.0	6.8
12	OVCz	3.3	5.0	1
13	P(VCz–St)	3.8	5.0	1
14	PVCz	4.2	5.0	$<10^{-2}$[d]

[a] Experiments 8–11 are measured in MeCN, whereas no. 12–14 are measured in DMF solvent. [b] D_2 is DMASt; A is DMTP. [c] This system is the same as system 2 in Table I. [d] The maximum value estimated by the experimental accuracy.

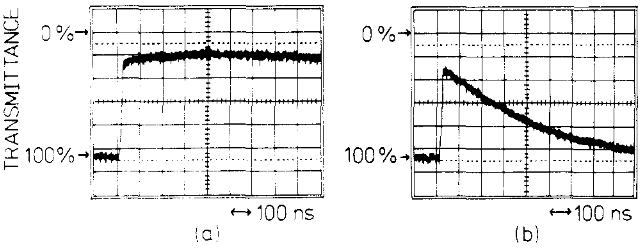


Figure 1. Oscillograms of transient absorption decay of $EtCz^{\bullet+}$ at its peak wavelength (780 nm) in cation radical transfer systems in MeCN: (a) EtCz–DMTP; (b) EtCz–DMASt–DMTP. For the concentration, see Table I.

D. Electrochemical Measurements. The oxidation potentials of EtCz and the cation radical acceptors were measured by cyclic voltammetry. The reference electrode Ag/0.01 N Ag^+ in MeCN was employed. The potentials were converted to the ones versus SCE ($E_{1/2}$): $E_{1/2}$ = 1.18 V for EtCz, 1.06 V for DMI, 0.99 V for TPA, 0.95 V for DPA, 0.77 V for DMA, 0.72 V for DMT, 0.64 V for DMASt, and 0.14 V for TMPD.

E. Cation Radical Transfer Measurements. At first a standard relationship between k_{tr} and the free energy change ($\Delta G°$) of the cation radical transfer for low molecular weight compounds was measured as a reference. The rate constant k_{tr} from $EtCz^{\bullet+}$ to D_2 was measured by the laser photolysis. Figure 1 shows the oscillograms of the transient absorption decay for the EtCz (D_1) systems at 780 nm (the peak wavelength of the absorption band of $EtCz^{\bullet+}$). Oscillogram (a) shows the decay of $EtCz^{\bullet+}$ for the EtCz–DMTP system at 780 nm: the absorption scarcely decays by the recombination of $EtCz^{\bullet+}$ ($D_1^{\bullet+}$) with $DMTP^{\bullet-}$ ($A^{\bullet-}$) in this time region. Oscillogram (b) shows the decay of $EtCz^{\bullet+}$ for the EtCz–DMASt–DMTP system (no. 2 in Table I) at the same wavelength: the decay is accelerated. The rate constant k_{tr} from $EtCz^{\bullet+}$ to DMASt was determined to be 11.0

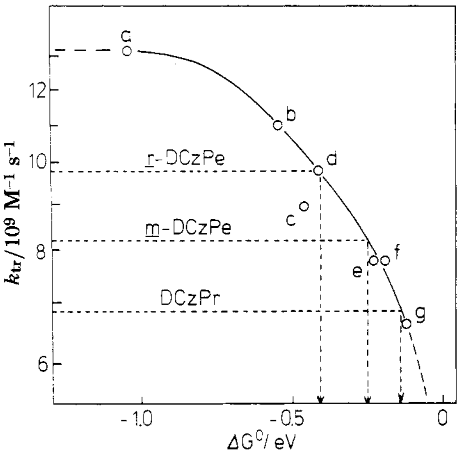


Figure 2. Relation between k_{tr} and $\Delta G°$ in the cation radical transfer process from $EtCz^{•+}$ to D_2: (a) $EtCz^{•+} \rightarrow$ TMPD (system 1); (b) $EtCz^{•+} \rightarrow$ DMASt (system 2); (c) $EtCz^{•+} \rightarrow$ DMT (system 3); (d) $EtCz^{•+} \rightarrow$ DMA (system 4); (e) $EtCz^{•+} \rightarrow$ DPA (system 5); (f) $EtCz^{•+} \rightarrow$ TPA (system 6); (g) $EtCz^{•+} \rightarrow$ DMI (system 7). In the case of the dimer model compounds, $\Delta G°$ of the cation radical transfer to DMASt was evaluated from k_{tr} as shown by the dotted lines (see text).

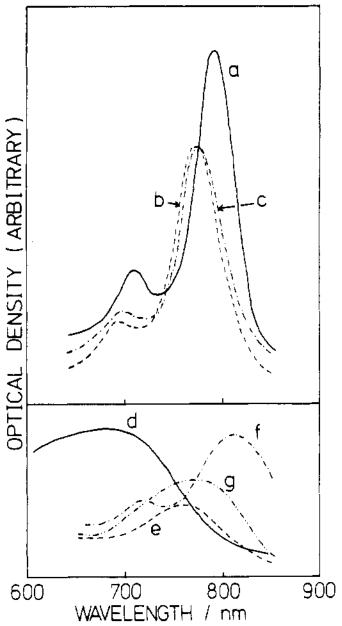


Figure 3. Transient absorption spectra of Cz cation radicals of various compounds (D_1) measured by the nanosecond laser photolysis at 298 K: (a) EtCz–DMTP (1.0×10^{-2} M) in MeCN; (b) *m*-DCzPe–DMTP (1.0×10^{-2} M) in MeCN; (c) DCzPr–DMTP (1.0×10^{-2} M) in MeCN; (d) *r*-DCzPe–DMTP (1.5×10^{-2} M) in MeCN; (e) PVCz–DMTP (5.0×10^{-2} M) in DMF; (f) P(VCz–St)–DMTP (2.0×10^{-2} M) in DMF; (g) OVCz–DMTP (1.0×10^{-2} M) in DMF. The optical density of Cz chromophore at 347 nm is about unity.

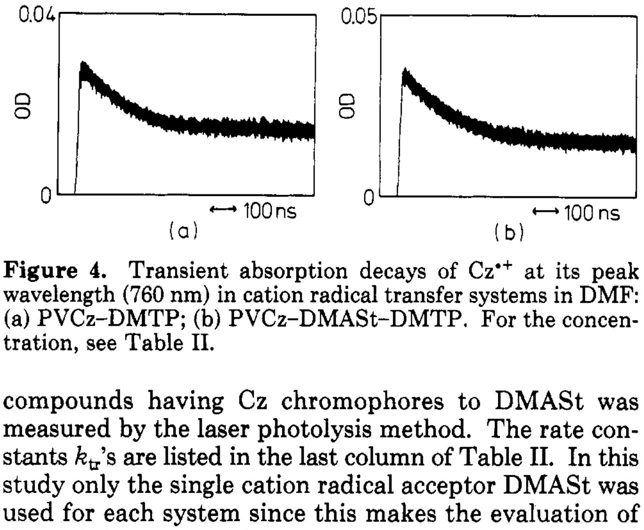


Figure 4. Transient absorption decays of $Cz^{•+}$ at its peak wavelength (760 nm) in cation radical transfer systems in DMF: (a) PVCz–DMTP; (b) PVCz–DMASt–DMTP. For the concentration, see Table II.

$\times 10^9$ M^{-1} s^{-1} by the slope in ln OD versus time plot (eq 7) since the rate of the cation radical transfer from $EtCz^{•+}$ to DMASt is much faster than that of the recombination of $EtCz^{•+}$ with $DMTP^{•-}$. The rate constant k_{tr} for other systems was also determined in the same way. Table I shows the results. These k_{tr}'s were confirmed by simulating the rise of $D_2^{•+}$ except for the EtCz–DMI–DMTP system in which no absorption of $DMI^{•+}$ could be observed.

The free energy change ($\Delta G°$) of the cation radical transfer from $EtCz^{•+}$ to D_2 is obtained by the difference between the oxidation potential of EtCz and that of the cation radical acceptor:

$$\Delta G° = E_{1/2}(D_2/D_2^{•+}) - E_{1/2}(D_1/D_1^{•+}) \qquad (8)$$

where $E_{1/2}(D_2/D_2^{•+})$ and $E_{1/2}(D_1/D_1^{•+})$ are the oxidation potentials of D_2 and D_1, respectively.

Figure 2 shows the relationship between k_{tr} and $\Delta G°$. In the region $\Delta G° < -0.9$ eV, the rate constant k_{tr} is diffusion-controlled, and in the region $\Delta G° > -0.9$ eV, k_{tr} decreases with increasing $\Delta G°$. Experimental values give a smooth curve which is expected for the electron-transfer reaction, though point C slightly deviates from the curve. On the basis of this standard relationship, $\Delta G°$ for the stabilized systems is estimated by measuring the transfer rate constant k_{tr}.

Results

A. Transient Absorption Spectra. Figure 3 shows the transient absorption spectra of cation radicals for various compounds that have Cz chromophores (D_1). The cation radical $EtCz^{•+}$ has an absorption band at ca. 780 nm[25] (Figure 3a). Transient absorption bands appear around 760 nm for *m*-$DCzPe^{•+}$ (Figure 3b) and 770 nm for $DCzPr^{•+}$ (Figure 3c), and the molar extinction coefficients for both *m*-$DCzPe^{•+}$ and $DCzPr^{•+}$ are slightly weaker than that for $EtCz^{•+}$. *m*-DCzPe and DCzPr have been shown to form a sandwich dimer cation radical.[17] The transient absorption band for *r*-$DCzPe^{•+}$ is very broad at ca. 710 nm (Figure 3d). This compound is known to form a second dimer cation radical.[17] Further, the transient absorption band of $Cz^{•+}$ in PVCz is very weak compared with that of $EtCz^{•+}$ and its peak is around 750 nm[19,20] (Figure 3e). The transient absorption band for $Cz^{•+}$ in P(VCz–St) is less broad than that of $PVCz^{•+}$ and its peak wavelength is at 820 nm (Figure 3f). The cation radical $Cz^{•+}$ in OVCz has a broad absorption band which is the same as that for $Cz^{•+}$ in PVCz (Figure 3g).

B. Cation Radical Transfer Systems. The cation radical transfer rate from the cation radical of various compounds having Cz chromophores to DMASt was measured by the laser photolysis method. The rate constants k_{tr}'s are listed in the last column of Table II. In this study only the single cation radical acceptor DMASt was used for each system since this makes the evaluation of the stabilization much easier. The rate constant k_{tr} decreases in the following order: 9.8×10^9 M^{-1} s^{-1} for *r*-DCzPe, 8.2×10^9 M^{-1} s^{-1} for *m*-DCzPe, and 6.8×10^9 M^{-1} s^{-1} for DCzPr, whereas k_{tr} from $EtCz^{•+}$ to DMASt is 11.0 $\times 10^9$ M^{-1} s^{-1}.

The rate constants k_{tr}'s for systems no. 12 and 13 were determined by simulating the absorption decays of $Cz^{•+}$, $DMASt^{•+}$, and $DMTP^{•-}$ by using eq 4–6, since the rate constants for these systems are small. The rate constants k_{tr}'s for the OVCz and P(VCz–St) are ca. 10^9 M^{-1} s^{-1}.

Figure 4 shows the decays for the PVCz systems. Decays (a) and (b) show the transient absorptions of the Cz cation radical for the PVCz–DMTP system and for the PVCz–DMASt–DMTP system (no. 14 in Table II), respectively. The transient absorption decay did not change even in the presence of DMASt. Therefore, considering the accuracy of the measurement, the k_{tr} of the cation radical transfer from $Cz^{•+}$ in PVCz to DMASt was estimated to be less than 10^7 M^{-1} s^{-1}.

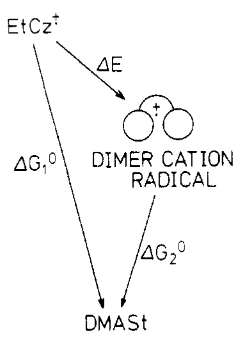


Figure 5. $\Delta G°$ from $EtCz^{\bullet+}$ and dimer cation radical to DMASt.

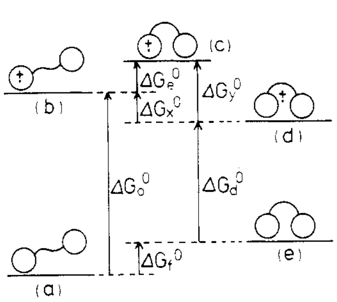


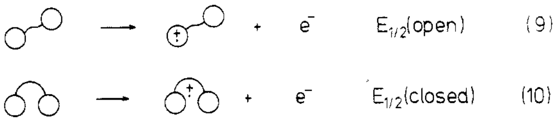
Figure 6. Scheme of formation of dimer cation radical: (a) ground state of open form; (b) localized cation radical of open form; (c) localized cation radical of closed form; (d) dimer cation radical; (e) ground state of closed form.

Discussion

A. Stabilization of Dimer Cation Radical. As shown in Table II, the rate constants k_{tr}'s decrease in the order $EtCz^{\bullet+}$ ($11.0 \times 10^9\ M^{-1}\ s^{-1}$), r-$DCzPe^{\bullet+}$ ($9.8 \times 10^9\ M^{-1}\ s^{-1}$), m-$DCzPe^{\bullet+}$ ($8.2 \times 10^9\ M^{-1}\ s^{-1}$), and $DCzPr^{\bullet+}$ ($6.8 \times 10^9\ M^{-1}\ s^{-1}$). This decrease is considered to be due to the stabilization of $Cz^{\bullet+}$ by the neighboring interaction with the other Cz chromophore in the dimer model compounds. Figure 5 shows that when $Cz^{\bullet+}$ is stabilized by the formation of the dimer cation radical, the free energy change ($\Delta G_2°$) of the cation radical transfer from the dimer cation radical to DMASt becomes less exothermic than that from $EtCz^{\bullet+}$ to DMASt. Then, the rate constant k_{tr} decreases with the decrease of exothermicity ($-\Delta G°$). The magnitude of such stabilization energy (ΔE) of $Cz^{\bullet+}$ is related to the conformation of two Cz chromophores, i.e., the extent of overlap between two Cz chromophores. Both DCzPr and m-DCzPe are known to form sandwich dimer cation radicals in which the two Cz chromophores have a total overlapping conformation, while r-DCzPe forms the second dimer cation radical with a partially overlapping conformation. Therefore, the order for k_{tr}'s suggests that the sandwich dimer cation radicals with a completely overlapping conformation are stabilized more strongly than the second dimer cation radical with a partially overlapping conformation.

B. Thermodynamic Consideration of the Stabilization Energy. In the ground state, dimer model compounds have such conformations that the steric hindrance is minimized: m-DCzPe and r-DCzPe have mainly TG and TT conformation, respectively,[30] and DCzPr has a conformation such that the two Cz chromophores are farthest apart. These conformations will be called the "open form" hereafter. When a cation radical of Cz chromophore is photochemically produced, it is stabilized by interaction with the neighboring chromophore to form the dimer cation radical where two Cz chromophores overlap with each other. Such a conformation of the dimer cation radical will be called the "closed form". In the case of DCzPr and m-DCzPe, it corresponds to the completely overlapping conformation. In the case of r-DCzPe, it corresponds to the partially overlapping conformation in which two Cz chromophores approach a little more closely each other than those in TT conformation of the ground state. Figure 6 shows a scheme to consider the stabilization of dimer cation radicals as described above. State (a) is in a ground state with an open form. State (b) is a localized cation radical with an open form: a cation radical which is free from the neighboring interaction will be called a "localized cation radical" and distinguished from the dimer cation radical. State (d) is a dimer cation radical, which can be observed by nanosecond laser photolysis. State (e) is a ground-state dimer (a closed form) formed immediately after the cation radical transfer from (d) to D_2. A localized cation radical with closed form (c) is assumed as a transition state in the course of formation of (d) from (b). In this manner, it is supposed that first the conformation changes, and then, a dimer cation radical is formed by the neighboring interaction. Figure 6 shows the free energy change ($\Delta G°$) between individual states. $\Delta G_e°$ is a free energy change when state (b) goes to the state (c) by a conformational change and is considered to be mainly caused by the entropy term. $\Delta G_y°$ corresponds to an enthalpy term of the charge delocalization since the conformation is held. Therefore, $\Delta G_x{}^0$ is a free energy change when a dimer model compound forms state (d) from state (b) and its entropy term and enthalpy term are considered to correspond to $\Delta G_e°$ and $\Delta G_y°$, respectively.

The cation radical transfer from the dimer cation radical (d) to D_2 is considered to be much faster than the conformational change from the closed form (e) to the open form (a). Then the rate constants of the cation radical transfer are considered to depend on $\Delta G_d°$ and not to depend on $\Delta G_f°$. Therefore, the stabilization energy of the dimer cation radical corresponds to the difference between $\Delta G_o°$ and $\Delta G_d°$. When the oxidation potentials of the open form (eq 9) and the closed form (eq 10) are measured, $\Delta G_o°$ and $\Delta G_d°$ can be calculated from these oxidation potentials.



The oxidation potential of the open form is taken to be equal to that of EtCz since the neighboring interaction can be neglected. Then, the stabilization energy (ΔE) can be estimated by the difference between the oxidation potential of EtCz and that of the closed form (eq 11).

$$\Delta E = \Delta G_d° - \Delta G_o° = E_{1/2}(\mathrm{open}) - E_{1/2}(\mathrm{closed}) = E_{1/2}(EtCz/EtCz^{\bullet+}) - E_{1/2}(\mathrm{closed}) \tag{11}$$

On the other hand, $\Delta G_f°$ is assumed to be equal to $\Delta G_e°$ since both are the conformational energies between the open form and the closed form, though their states are different: one is the state of the cation radical and the other is the neutral state. Therefore, from another viewpoint the stabilization energy $\Delta G_o° - \Delta G_d°$ is considered to be equal to $\Delta G_x° + \Delta G_e°$ ($=\Delta G_y°$). That is, it corresponds to the enthalpy term in the process from the localized cation radical to the dimer cation radical.

C. Stabilization Energy of Dimer Model Compounds. 1. Oxidation Potentials in the Closed Form. Equation 11 shows that the stabilization energy of dimer cation radicals can be estimated if the oxidation potential of the closed form of the dimer model compounds are obtained. The oxidation potential measured by cyclic

Table III
Oxidation Potential and Stabilization Energy of Dimer Model Compounds

compd	$\Delta G°$/eV	$E_{1/2}$(closed)/V	ΔE/eV
EtCz	–0.54[a]	1.18	
r-DCzPe	–0.41	1.05	0.13
m-DCzPe	–0.24	0.88	0.30
DCzPr	–0.13	0.77	0.41

[a] This value was calculated from the oxidation potentials of EtCz and DMASt.

voltammetry, however, corresponds to that of the open form ($E_{1/2}$(open)) and not to $E_{1/2}$(closed). Therefore direct evaluation of $E_{1/2}$(closed) is impossible. The free energy change ($\Delta G°$) of the cation radical transfer is related to the difference between the oxidation potential of a dimer model compound and that of DMASt by eq 8. Therefore, the oxidation potential ($E_{1/2}$(closed)) of a dimer model compound in the closed form can be estimated from $\Delta G°$ by using the following equation:

$$E_{1/2}(\text{closed}) = E_{1/2}(\text{DMASt}/\text{DMASt}^{\bullet +}) - \Delta G° = 0.64 - \Delta G° \tag{12}$$

In this study, $\Delta G°$ was estimated by using the relation between $\Delta G°$ and k_{tr} for low molecular weight compounds (Figure 2). In Figure 2 $\Delta G°$ was obtained from the transfer rate constant k_{tr} in the ordinate as shown by the dotted lines. The values of $\Delta G°$ and of $E_{1/2}$(closed) are shown in the second and third columns in Table III, respectively.

The oxidation potential $E_{1/2}$(closed) decreases in the order *r*-DCzPe (1.05 V versus SCE), *m*-DCzPe (0.88 V versus SCE), and DCzPr (0.77 V versus SCE), whereas that of EtCz is 1.18 V versus SCE. This shows that the oxidation potential decreases with the increase of the stabilization by the neighboring interaction.

Beens and Weller[31] investigated the oxidation potential of dimers by the emission spectra of the D–D–A exterplex. They have estimated the oxidation potential of the naphthalene dimer using eq 13, where $E_{1/2}(\text{D}/\text{D}^+)$ and

$$E_{1/2}(\text{D}/\text{D}^+) - E_{1/2}(\text{DD}/\text{DD}^+) = \nu'_{\max} - \nu''_{\max} \tag{13}$$

$E_{1/2}(\text{DD}/\text{DD}^+)$ are the oxidation potentials of monomer and dimer, respectively, and $\nu'_{\max}$ and $\nu''_{\max}$ are the wavenumbers of the peaks of D–A exciplex emission and D–D–A exterplex emission, respectively. Later, Masuhara et al. applied this method to the DCzPe–1,2-dicyanobenzene system.[32] In the present study, we tried to estimate the oxidation potential of the dimer model compounds by applying this equation to the dimer model compound–DMTP systems in benzene. The values $E_{1/2}(\text{D}/\text{D}^+)$ and $\nu'_{\max}$ are taken from the oxidation potential of EtCz and the wavenumber of the peak of exciplex emission in the EtCz–DMTP system, respectively. The peak wavelength of the exterplex emission in the dimer model compound–DMTP systems is about 520 nm for *r*-DCzPe, 560 nm for *m*-DCzPe, and 550 nm for DCzPr, whereas the exciplex in the EtCz–DMTP system appears at ca. 480 nm. Then, the oxidation potentials of the dimer model compounds are estimated to be ca. 0.99 V for *r*-DCzPe, 0.81 V for *m*-DCzPe, and 0.85 V for DCzPr. These values agree within ±0.1 V with those estimated by the rate constants of the cation radical transfer mentioned above.

2. Estimate of Stabilization Energy. Equation 11 shows that the stabilization energy (ΔE) corresponds to the difference between the oxidation potential (1.18 V) of EtCz measured by cyclic voltammetry and that ($E_{1/2}$(closed)) of the dimer model compounds in the closed form listed in Table III. Thus, by using the values $E_{1/2}$(closed) in Table III, ΔE can be calculated. The obtained values of ΔE are listed in the last column in Table III: ca. 0.1 eV for *r*-DCzPe, 0.3 eV for *m*-DCzPe, and 0.4 eV for DCzPr. This shows that the stabilization of the dimer cation radicals is closely related to the overlappoing of the two Cz rings and that the stabilization energies are 0.3–0.4 eV and 0.1 eV for the sandwich dimer cation radical and the second dimer cation radical, respectively.

D. Stabilization of the Cation Radical Formed in PVCz. As shown in Table II, cation radical transfer from $\text{Cz}^{\bullet +}$ in PVCz to DMASt could not be observed (no. 14). This suggests that $\text{Cz}^{\bullet +}$ in PVCz is stabilized more than the dimer cation radicals ($\Delta E \simeq 0.1–0.4$ eV). Washio et al.[21] studied the reactivity of the Cz cation radical in PVCz by pulse radiolysis and reported that the $\text{Cz}^{\bullet +}$ in PVCz is not transferred to DPA or DMA because of its stabilization by the neighboring interaction but that a stronger donor such as *N,N,N′,N′*-tetramethylbenzidine need participate in the cation radical transfer.

In general, the rate constant of electron transfer decreases slowly with the increase of $\Delta G°$ in the exothermic region and drops rapidly at ca. $\Delta G° = 0$.[33] Since the cation radical transfer process in this study is an electron transfer process, k_{tr} is considered to decrease rapidly around $\Delta G° = 0$ and such a tendency is observed in Figure 2. The free energy change ($\Delta G°$) of the cation radical transfer from $\text{Cz}^{\bullet +}$ in PVCz to DMASt is considered not to be less than $\Delta G° = 0$. Therefore, the stabilization energy of $\text{Cz}^{\bullet +}$ in PVCz is estimated to be at least 0.5–0.6 eV or more because $\Delta G°$ from $\text{EtCz}^{\bullet +}$ to DMASt is –0.54 eV. The cation radical $\text{Cz}^{\bullet +}$ in PVCz is expected to have a stronger neighboring interaction, e.g., larger delocalization, than the dimer cation radicals due to high local concentration of Cz chromophores and this is verified by the fact that its transient absorption band is much broader than those of the dimer cation radicals. However, the stabilization cannot be explained by the neighboring interaction alone. The cation radical transfer to DMASt is observed for OVCz, though it may have almost the same neighboring interaction as PVCz. As for P(VCz–St), the cation radical transfer to DMASt is observed with k_{tr} on the order of 10^9 M^{-1} s^{-1}. The cation radical transfer is suppressed, but not so much as for PVCz. The copolymer is considered not to have any interaction between Cz chromophores in the polymer chain since the fraction of Cz unit is about 10 mol % and excimer emission is not observed in nonpolar solvents. Hence, the suppression of cation radical transfer is presumably due to the steric hindrance of the polymer chain to the access of a cation radical acceptor. The fact that the cation radical $\text{Cz}^{\bullet +}$ in PVCz is hardly transferred to DMASt is probably caused by the steric hindrance of the polymer chain as well as the neighboring interaction.

Conclusion

The cation radical transfer from the cation radical of PVCz, P(VCz–St), OVCz, the dimer model compounds, and EtCz to a cation radical acceptor DMASt was measured by the nanosecond laser photolysis. In the case of PVCz, cation radical transfer to DMASt could not be observed. The cation radicals of P(VCz–St) and OVCz are transferred to DMASt with a k_{tr} on the order of 10^9 M^{-1} s^{-1}. The dimer cation radicals of the dimer model compounds were stabilized by the neighboring interaction in the order *r*-DCzPe, *m*-DCzPe, and DCzPr, and their stabilization energies were estimated to be ca. 0.1, 0.3, and 0.4 eV, respectively. This shows that the sandwich dimer cation radical in which the two Cz chromophores overlap totally is stabilized more strongly than the second dimer cation radical in which the Cz chromophores overlap only partially. Further, Cz cation radical in PVCz is considered to be more stabilized than the cation radicals of these dimer model compounds and its stabilization energy is more than 0.5–0.6 eV.

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Registry No. EtCz, 86-28-2; DCzPr, 25837-66-5; *r*-DCzPe, 80039-85-6; *m*-DCzPe, 80039-86-7; PVCz, 25067-59-8; (VCz)(St) (copolymer), 26710-15-6; DMTP, 120-61-6; DCNB, 91-15-6; DMASt, 2039-80-7; DMT, 99-97-8; DMA, 121-69-7; TMPD, 100-22-1; DPA, 122-39-4; TPA, 603-34-9; DMI, 875-79-6.

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