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Remarkable 3-methyl substituent effects on the cyclization reaction of diphenylamine derivative cation radicals in acetonitrile†

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Reactions of methyl substituted diphenylamine cation radicals in acetonitrile were observed using an electron transfer stopped-flow (ETSF) method. In the reactions of the 4-methylphenyl(phenyl)amine cation radical (4M–DPA$^{\bullet+}$), the main reaction route was the formation of the benzidine dimer, which is similar to the case of the diphenylamine cation radical (DPA$^{\bullet+}$). The dimerization rate of 4M–DPA$^{\bullet+}$ was 2.3×10^4 M^{-1} s^{-1}, which was slower than for DPA$^{\bullet+}$ (dimerization rate 1.0×10^6 M^{-1} s^{-1}), due to the 4-methyl substituent. Also, in the cases of 4-methyl and 4,4′-dimethyl DPA$^{\bullet+}$, the formation of the cyclized dimer compounds was inferred from the presence of a large excess of the neutral molecules acting as a base. In contrast, the formation of the cyclized dimer compounds was characterized for 3-methyl- and 3,3′-dimethyl substituted DPA$^{\bullet+}$ using cyclic voltammetry. In the ETSF method, the dimerization reaction was determined to be second-order in the cation radical and totally independent of the neutral molecule. The dimerization rates were *ca.* 1.0×10^7 M^{-1} s^{-1}, which are faster than the reaction of DPA$^{\bullet+}$. In spite of the complex pathway of the cyclization reaction, the 3-methyl substituent was found to promote the reaction between the 6-position of the phenyl ring and the nitrogen molecule of 3M–DPA$^{\bullet+}$ or 3,3′M–DPA$^{\bullet+}$.

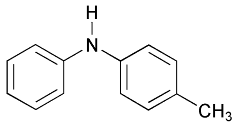
Introduction

Substituent effects on the reaction kinetics of the triphenylamine derivative cation radicals (X–TPA$^{\bullet+}$) in acetonitrile (AN) have been studied previously by Nelson and coworkers.[1] Systematic changes in the dimerization rate constants of X–TPA$^{\bullet+}$ were measured electrochemically, and the results were compared with Hammett parameters.[1]

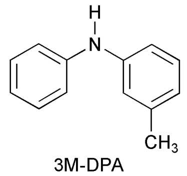
The low reactivity of X–TPA$^{\bullet+}$ in AN as well as the unaltered reaction route to form the dimer tetraphenylbenzidine derivatives enabled such a kinetic study to be followed. For some diphenylamine derivative cation radicals (X–DPA$^{\bullet+}$), which are much more unstable than X–TPA$^{\bullet+}$, the details of the reaction processes can now be analyzed using new detection methods, *e.g.* scanning cyclic voltammetry.[2–4] Thus, little is known about the substituent effects on the reaction kinetics of such short-lived cation radicals such as X–DPA$^{\bullet+}$.[4]

In considering the substituent effects on the kinetics of the reactions of cation radicals electrochemically generated in aprotic solvents, in some cases, substituents may just alter the reactivity of a particular reaction without altering the reaction route. Typical examples are the dimerization reaction of X–TPA$^{\bullet+}$ [1] and the nucleophilic reactions of the 9-substituted-10-phenylanthracene cation radicals.[5] In contrast, in other cases, substituents can change the reaction routes to bring different products, as successfully shown for the reactions of the 9-substituted anthracene cation radicals.[6] Or, the substituents might change only the reaction route although the final products are similar.[7] Because of the variety and complexity of the reactions of cation radicals,[8] it would be necessary to carry out further extensive studies, in particular, on the short-lived cation radicals to elucidate the effects of the substituents in detail.

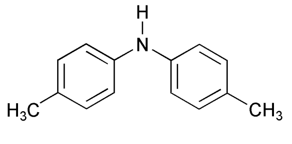
In the present paper, we thus observed the substituent effects on the reaction kinetics of X–DPA$^{\bullet+}$. Focusing on the methyl substituent here, we analyzed the decay reactions of the cation radicals of four derivatives, *i.e.* 4-methylphenyl(phenyl)amine (4M–DPA), bis(4-methylphenyl)amine (4,4′M–DPA), 3-methylphenyl(phenyl)amine (3M–DPA)and bis(3-methylphenyl)amine (3,3′M–DPA).



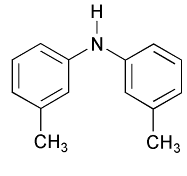
4M-DPA



3M-DPA



4,4′M-DPA



3,3′M-DPA

For the reactions of the 4-monosubstituted and 4,4′-disubstituted DPA$^{\bullet+}$, Serve and coworkers revealed different reaction pathways, *i.e.* the formation of four different types of dimers having benzidine, dihydrodiphenylphenazine, *p*-phenylenediamine and hydrazine moieties, depending on the bases coexisting in AN solutions.[9–11] Additionally, to analyze the cyclization mechanism to form the dihydrodiphenylphenazine type dimer in more detail, the electrochemical oxidation behavior of *N,N,N′*-triphenyl-*o*-phenylenediamine was

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† Electronic supplementary information (ESI) available: results of kinetic analysis for the reactions in Figs. 4 and 5. See http://www.rsc.org/suppdata/p2/b2/b201796b/

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investigated by Berkenkotter and Nelson.[12] However, kinetic studies of the reaction processes have not been carried out.

In the present work, for the kinetic analysis of the decay processes of the methyl-substituted $DPA^{\bullet+}$, we used an electron transfer stopped-flow (ETSF) method,[13–19] to analyze the dimerization of $DPA^{\bullet+}$ successfully.[13,14] In this method, unstable cation radicals ($N^{\bullet+}$) are formed *via* the electron transfer with long-lived cation radicals ($M^{\bullet+}$). Thus, when the redox potential of the $M^{\bullet+}/M$ couple is positive to that of the $N^{\bullet+}/N$ couple, the electron transfer reaction of eqn. (1) should be favorable thermodynamically.

$$N + M^{\bullet+} \longrightarrow N^{\bullet+} + M \qquad (1)$$

Thus, by mixing the solutions of N and $M^{\bullet+}$, we can form $N^{\bullet+}$ *via.* eqn. (1), initiate the reaction of $N^{\bullet+}$ and investigate the decay reaction of $N^{\bullet+}$, spectroscopically. The detection ability of the ETSF method is comparable to fast scanning cyclic voltammetry with the scan rates over 1000 V s^{-1}.[19]

Experimental

For the stopped-flow measurements, a rapid-scan stopped-flow spectroscopic system, RSP-601 (Unisoku Co. Ltd., Hirakata, Japan), was used. Using this apparatus, dynamic transformation of absorption spectra can be observed with a minimized time interval of 1.0 ms after mixing two solutions.

All the measurements were carried out in AN as the solvent. As a substrate to form the persistent cation radicals, $M^{\bullet+}$, in eqn. (1), tris(*p*-bromophenyl)amine (TBPA) was used. While AN solutions of $TBPA^{\bullet+}$ were prepared using the electrochemical oxidation as in our previous work,[13–18] the commercially available hexachloroantimonate salt of $TBPA^{\bullet+}$ (Aldrich) was used as received. The effect of the counter anions, ClO_4^-, PF_6^- or $SbCl_6^-$, is expected to be very small for the ETSF measurements. Actually, no difference from the previous results was confirmed by observing the reaction of $DPA^{\bullet+}$ generated using the $SbCl_6^-$ salt of $TBPA^{\bullet+}$.

In the present ETSF experiments, an AN solution of $TBPA^{\bullet+}$ was mixed with an AN solution containing the DPA derivatives. Because the oxidation potentials of all the derivatives were negative compared to that of TBPA, the target cation radicals were formed successfully after the mixing, and the decay processes could be followed by observing the time changes in absorption spectra.

For all substrates, the available chemicals of high purity, and the dehydrated acetonitrile (AN) (Wako chemicals) were used as received.

Results and discussion

Decay reaction of 4-methylphenyl(phenyl)amine cation radical

At first, the decay reactions of 4M–$DPA^{\bullet+}$ were observed using the ETSF method by generating 4M–$DPA^{\bullet+}$ *via* the electron transfer reaction of eqn. (2).

$$4M\text{–}DPA + TBPA^{\bullet+} \longrightarrow 4M\text{–}DPA^{\bullet+} + TBPA \qquad (2)$$

Fig. 1(A) shows the time-resolved absorption spectra observed after mixing an AN solution of 0.10 mM 4M–DPA with an AN solution of 0.10 M $TBPA^{\bullet+}$. Just after the mixing, the absorption of $TBPA^{\bullet+}$ at 705 nm totally disappeared and a new absorption maximum was observed at 689 nm, which verifies the quantitative completion of eqn. 2 in the mixing part before stopping the solutions. In this experiment, the concentration of 4M–$DPA^{\bullet+}$ and TBPA instantaneously formed after the mixing is 0.050 mM, taking into account the dilution due to mixing. In the ETSF method, it is characteristic that the solution containing only cation radicals can be formed in the absence of the precursor molecules.[15,16]

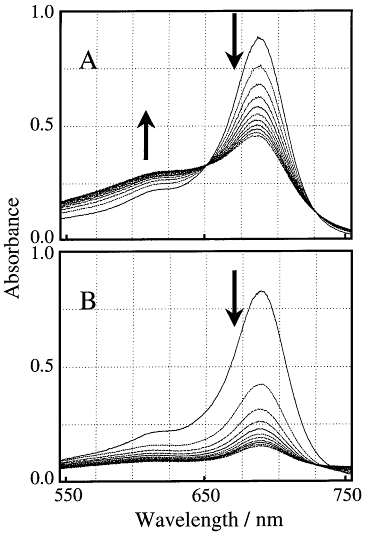


Fig. 1 Time-resolved absorption spectra recorded after an AN solution of 4M–DPA was mixed with an AN solution of 0.10 mM $TBPA^{\bullet+}$; concentration of 4M–DPA: (A) 0.10, (B) 10 mM. Time interval of each spectrum 200 ms.

When 4M–$DPA^{\bullet+}$ is quantitatively formed without 4M–DPA in this manner, the spectral changes showed the decrease of the absorption at 689 nm together with an increase in the absorption around 600 nm, as shown in Fig. 1A, which has two isosbestic points.

This spectral change can be assigned to the formation of the dication of the dimer benzidine compound, bis(4-methylphenyl)benzidine (4,4′M–DPB^{2+}), as expressed by eqn. (3), which is the same as in the case of $DPA^{\bullet+}$ without DPA.[14]

$$4\,(4M\text{–}DPA^{\bullet+}) \longrightarrow 4{,}4'M\text{–}DPB^{2+} + 2(4M\text{–}DPA) + 2H^+ \qquad (3)$$

The value of the absorption maximum of 4,4′M–DPB^{2+} (640 nm)[11] is in good agreement with the present result.

Compared with the results of $DPA^{\bullet+}$,[14] the decay reaction of 4M–$DPA^{\bullet+}$ is much slower. Thus, the absorption spectrum of 4M–$DPA^{\bullet+}$ was easily characterized; the absorption maximum is 689 nm and the molar absorption coefficient is 2.0×10^4 $M^{-1}cm^{-1}$. The lower reactivity should be attributed to the effect of the 4-methyl substituent to block one reaction position for the dimerization.

In the reaction of $DPA^{\bullet+}$, when neutral DPA coexisted in the solution, it was found that DPA merely affected the equilibria involving the cation radical and dication of the dimer, diphenybenzidine (DPB).[14] The effects of the precursor molecules were also examined in the case of 4M–$DPA^{\bullet+}$ by mixing an AN solution of 0.10 mM $TBPA^{\bullet+}$ with an AN solution of 1.0 or 10 mM 4M–DPA.

Fig. 1(B) shows the decay process of 0.05 mM 4M–$DPA^{\bullet+}$ in the presence of 4.95 mM 4M–DPA. Compared with Fig. 1(A), a continuous decay of 4M–$DPA^{\bullet+}$ was observed without forming the species that absorb around this wavelength region. Although we observed the absorption spectra from 350 nm to 900 nm, in addition to the wavelengths covered in Fig. 1(B), the formation of a cation radical species was not observed, while $DPB^{\bullet+}$ was formed in the case of $DPA^{\bullet+}$.[14] A similar occurrence was noted with 0.05 mM 4M–$DPA^{\bullet+}$ in the presence of 0.45 mM 4M–DPA (data not shown). From the above results, when a 9-fold or 99-fold amount 4M–DPA was present, the amount of 4,4′M–DPB formed can be concluded to be much smaller than that formed without 4M–DPA. This is totally different from the previous case of DPA, in which an increase of neutral DPA was found to merely cause the transformation from DPB^{2+} to $DPB^{\bullet+}$.[14]

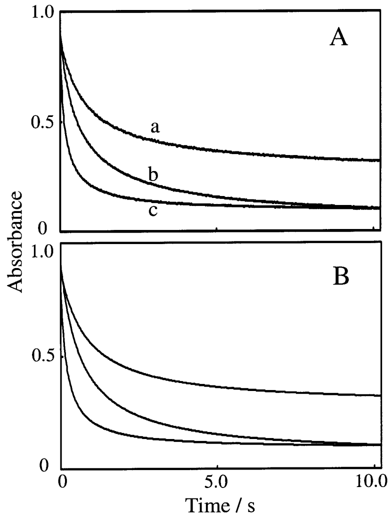


Fig. 2 (A) Changes in absorbance with time recorded after an AN solution of 4M–DPA was mixed with an AN solution of 0.10 mM TBPA$^{•+}$; concentration of 4M–DPA: (a) 0.10, (b) 1.0, (c) 10 mM. Wavelength of the measurement: 689 nm. (B) Simulated results for the three curves in (A), assuming second-order decay and subtracting the contribution of the background absorbance.

To discuss these differences between DPA$^{•+}$ and 4M–DPA$^{•+}$ in detail, Fig. 2(A) shows the changes in absorbance of 4M–DPA$^{•+}$ at 689 nm with time, recorded at the three concentrations of 4M–DPA mentioned above. Curve (a) represents the decay of 4M–DPA$^{•+}$ without 4M–DPA. In this case, the baseline can be attributed to the formation of the dication of the dimer compound, as observed also in the case of DPA.[14] Thus, by subtracting this contribution, the decay profile could be simulated as shown in Fig. 2(B). From the good agreement, the reaction order of 4M–DPA$^{•+}$ was determined to be second, *i.e.* $-d\,[4\text{M–DPA}^{•+}]/dt = k\,[4\text{M–DPA}^{•+}]^2$, with a rate constant, k, of 2.3×10^4 M^{-1} s^{-1}.

Because the dimerization rate constant of DPA$^{•+}$ was 1.0×10^6 M^{-1} s^{-1}, the 4-methyl substituent reduced the reaction rate to 1/43 presumably due to blocking and the electronic effects. In the case of TPA$^{•+}$, it was reported that one methyl substituent at the *para*-position reduced the dimerization rate constant to 1/133.[1]

In the presence of 0.45 mM and 4.95 mM 4M–DPA, the decay curves of 4M–DPA$^{•+}$ were recorded as (b) and (c), respectively. Also for these curves, simulation analysis was performed by subtracting the smaller background contribution. Consequently, the decay late law was found to be the same, *i.e.* $-d\,[4\text{M–DPA}^{•+}]/dt = k\,[4\text{M–DPA}^{•+}]^2$, and the rate constants were determined to be 2.9×10^4 and 9.7×10^4 M^{-1} s^{-1}, respectively.

This might imply the participation of [4M–DPA] into the rate law as the reaction of 1-aminopyrene cation radical.[15] However, this can be ruled out because the difference in the rate constants obtained without 4M–DPA and in the presence of 9-fold 4M–DPA is very small.

Thus, it is inferred that the reason for the changes in the time-resolved absorption spectra in Fig. 1 are the concerted decreases of 4M–DPA$^{•+}$ due to 4M–DPA, concurrent with the dimerization reaction shown in eqn. (3). It is known that bases promote the cyclization of 4M–DPA$^{•+}$.[9,10] Thus, assuming 4M–DPA functions as a base, we can account for the continuous decay of 4M–DPA$^{•+}$ in Fig. 1(B).

Decay reaction of bis(4-methylphenyl)amine cation radical

Next, we observed the decay process of 4,4′M–DPA$^{•+}$ in AN. Because two reaction active sites of DPA are blocked by the methyl substituents, 4,4′M–DPA$^{•+}$ was very stable in AN. Actually, the cyclic voltammogram of 4,4′M–DPA in AN could be recorded as reversible even at conventional scan rates. In the ETSF measurement as well, no decrease of 4,4′M–DPA$^{•+}$ was observed in the time domain of 10 s, when it was generated quantitatively without neutral 4,4′M–DPA through the equimolar mixing with TBPA$^{•+}$ (data not shown).

However, when 0.05 mM 4,4′M–DPA$^{•+}$ was generated in the presence of 4.95 mM 4,4′M–DPA, an apparent continuous decrease of 4,4′M–DPA$^{•+}$ was observed as shown in Fig. 3. This is a remarkable contrast to the absence of any decrease of 4,4′M–DPA$^{•+}$ without 4,4′M–DPA. For this decrease in Fig. 3, the appearance of different reaction routes due to the precursor 4,4′M–DPA is most probably expected. By working as a weak base, the neutral 4,4′M–DPA is expected to promote the cyclization reaction to form the dihydrophenazine dimer compound, as inferred in the case of 4M–DPA$^{•+}$. The function of the neutral molecules as a base has been reported recently.[18] The difference between the cases of 4M–DPA$^{•+}$ and 4,4′M–DPA$^{•+}$ is whether or not there is a route for the dimerization to form the diphenylbenzidine.

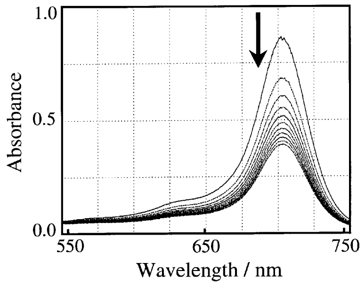


Fig. 3 Time-resolved absorption spectra recorded after an AN solution of 10 mM 4,4′M–DPA was mixed with an AN solution of 0.10 mM TBPA$^{•+}$. Time interval of each spectrum 200 ms.

Decay reaction of 3-methylphenyl(phenyl)amine and bis(3-methylphenyl)amine cation radicals

On the basis of the previous results of DPA$^{•+}$[14] and the above results of 4M–DPA$^{•+}$ and 4,4′M–DPA$^{•+}$, what can we expect for the reactions of 3M–DPA$^{•+}$ and 3,3′M–DPA$^{•+}$?

While the 3-methyl substituent might have some steric hindrance and/or electronic effects on the reactivity of the 4-position (*i.e. para*-position), the formation of the dimer diphenylbenzidine compounds would be expected because they have no definite blocking substituents on the 4- and 4′-positions. In particular, 3M–DPA$^{•+}$ has one simple phenyl ring for the dimerization through *para–para* coupling. Hence, the reaction processes of 3M–DPA$^{•+}$ and 3,3′M–DPA$^{•+}$ were observed similarly using the ETSF method.

Fig. 4 shows the changes in absorption spectra in the reactions of 3M–DPA$^{•+}$. While the increase of the absorption around 600 nm was observed when 0.05 mM 3M–DPA$^{•+}$ was quantitatively generated without 3M–DPA (Fig. 4(A)), a continuous decrease of 3M–DPA$^{•+}$ was observed when 0.05 mM 3M–DPA$^{•+}$ was generated in the presence of 4.95 mM 3M–DPA (Fig. 4(B)). This result is quite similar to the case of 4M–DPA$^{•+}$ as shown in Fig. 1. However, it is noticeable that the decay rates of 3M–DPA$^{•+}$ were much faster than those of 4M–DPA$^{•+}$; the time interval of each absorption spectrum is 200 ms in Fig. 1 and 4 ms in Fig. 4.

We performed the simulation analysis for the time changes in absorbance of 3M–DPA$^{•+}$ at 689 nm, observed in the two conditions shown in Fig. 4 (see the supplementary information†). As a result, in both cases, the reaction order of 3M–DPA$^{•+}$ and the decay rate (8.7×10^6 M^{-1} s^{-1}) were determined to be second-order.Thus, the reaction rate of 3M–DPA$^{•+}$ was found to be much higher than that of 4M–DPA$^{•+}$, and faster than that of DPA$^{•+}$.[14]

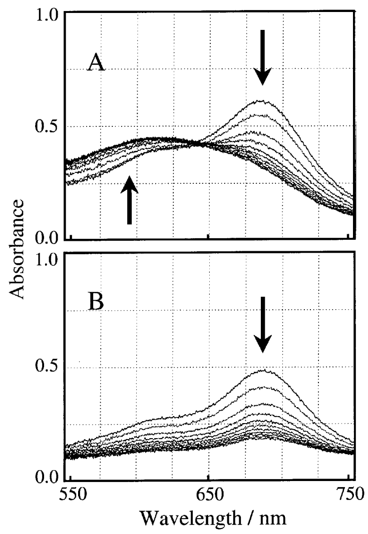


Fig. 4 Time-resolved absorption spectra recorded after an AN solution of 3M–DPA was mixed with an AN solution of 0.10 mM TBPA$^{•+}$; concentration of 3M–DPA: (A) 0.10, (B) 10 mM. Time interval of each spectrum 4 ms.

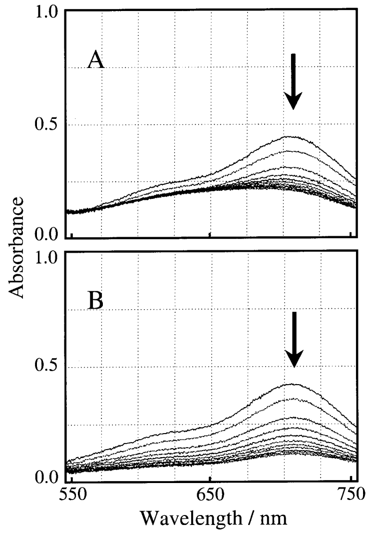


Fig. 5 Time-resolved absorption spectra recorded an AN solution of 3,3′M–DPA was mixed with an AN solution of 0.10 mM TBPA$^{•+}$; concentration of 3,3′M–DPA: (A) 0.10, (B) 10 mM. Time interval of each spectrum 4 ms.

Before discussing the effects of the 3-methyl substituent in detail, we present the results of similar kinetic measurements for 3,3′M–DPA$^{•+}$. Fig. 5 shows the changes in absorption spectra for the reactions of 3,3′M–DPA$^{•+}$ recorded under two conditions, *i.e.* without 3,3′M–DPA and in the presence of 4.95 mM 3,3′M–DPA. In both the cases, the decay profiles could be simulated assuming the second-order dependence of [3,3′M–DPA$^{•+}$] with a rate constant of 1.1×10^7 M^{-1} s^{-1} (see the supplementary information†). Thus, the reaction rate of 3,3′M–DPA$^{•+}$ was found to be a little faster than that of 3M–DPA$^{•+}$.

Mechanistic discrimination using cyclic voltammetry

The above kinetic results for the methyl derivatives seem to be a little curious, assuming a similar reaction route to form the diphenylbenzidine dimer as the case of DPA$^{•+}$. Thus, here we report the cyclic voltammograms of the present derivatives.

Fig. 6 shows the cyclic voltammograms of (A) DPA, (B) 4M–DPA, (C) 3M–DPA and (D) 3,3′M–DPA. The electrochemical measurement of 4,4′M–DPA showed a reversible one-electron oxidation response, while those for the others showed complex responses as in Fig. 6.

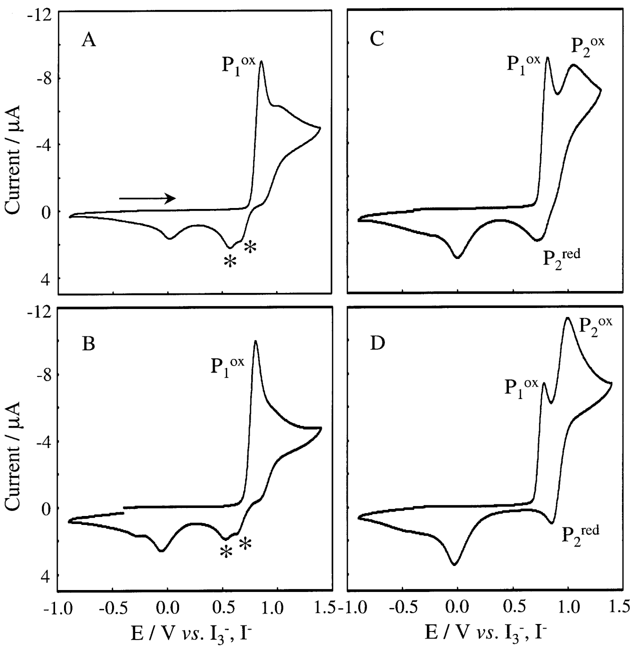
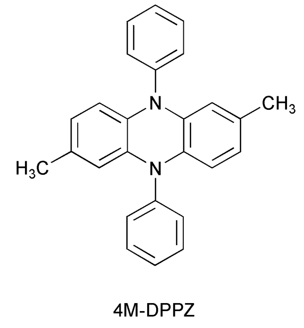


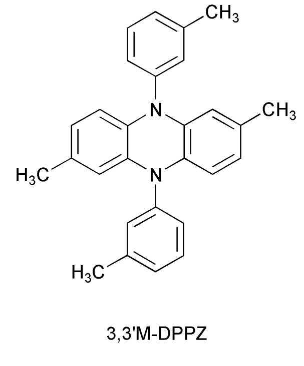
Fig. 6 Cyclic voltammograms of DPA derivatives in AN: (A) DPA, (B) 4M–DPA, (C) 3M–DPA and (D) 3,3′M–DPA. Working electrode; Pt disk electrode (diam 1.6 mm). Reference electrode; Pt/(I^-,I_3^-) electrode. Scan rate; 100 mVs^{-1}. Concentration of DPA derivatives 1.0 mM; supporting electrolyte 0.10 M $TBAPF_6$.

On interpreting these voltammograms, the most noticeable and significant point is the reduction peaks of the oxidation states of the dimer benzidine compounds marked by asterisk (*), which were observed only for DPA, and 4M–DPA. These two successive reduction peaks are evidence for the formation of the dimer diphenylbenzidine. In contrast, for 3M–DPA and 3,3′M–DPA, no such peaks were observed in these voltammograms. This was true even when the potential was reversed at the potential just positive to the first oxidation peak (P_1^{ox}).

By referring to previous studies by Serve and coworkers for the reactions of 4,4′M–DPA$^{•+}$[9] and Berkenkotter and Nelson to reveal the mechanism,[12] the present voltammetric results obtained for 3M–DPA and 3,3′M–DPA can be reasonably



4M-DPPZ



3,3′M-DPPZ

assigned to the formation of the cyclization dimer compounds, dihydrodiphenylphenazine derivatives, 3M–DPPZ (the structure is the same as 4M–DPPZ) and 3,3′M–DPPZ.

This is because the redox peaks (P_2) positive to the first oxidation of monomers (P_1) can be assigned to those of the cation radical/dication couples of 3M–DPPZ or 3,3′M–DPPZ judging from the voltammetric results obtained for similar derivatives,[9,12] in addition to the absence of reduction peaks of the diphenylbenzidine dimmers (*). The formation of the 3M–DPPZ and 3,3′M–DPPZ is also confirmed by the cyclic voltammetric measurement followed by the exhaust electrolysis as carried out previously.[12] Actually we carried out such measurements and confirmed that two couples of peaks could be attributed to the first and second reduction of the DPPZ derivatives.

In the case of 3M–DPA$^{\bullet+}$, the reaction mechanism to form 3M–DPPZ can be written as in eqs. (4)–(6) assuming the formation of the *N,N,N′*-triphenyl-*o*-phenylenediamine derivative (TPOPD) as the intermediate.[12]

$$2\,(\text{3M-DPA}^{\bullet+}) \xrightarrow{\text{slow}} \text{TPOPD} + 2\,\text{H}^+ \qquad (4)$$

$$\text{TPOPD} + 2\,(\text{3M-DPA}^{\bullet+}) \xrightarrow{\text{fast}} \text{3M-DPPZ} + 2\,(\text{3M-DPA}) + 2\,\text{H}^+ \qquad (5)$$

$$\text{3M-DPPZ} + \text{3M-DPA}^{\bullet+} \overset{K}{\rightleftarrows} \text{3M-DPPZ}^{\bullet+} + \text{3M-DPA} \qquad (6)$$

In this mechanism, on the basis of the second-order dependence of [3M–DPA$^{\bullet+}$] and no dependence on [3M–DPA], the initial interaction between the two 3M–DPA$^{\bullet+}$ can be regarded as the rate-determining step in eqn. (4), though the proton release process is unclear from the present kinetic results. However, the reaction in eqn. (5) is considered to be so fast so as not to be followed by [3M–DPA].

The spectral differences in Figs. 4 and 5 between (A) and (B) can be explained by the above mechanisms. As the oxidation potential of 3M–DPPZ$^{\bullet+}$ to the dication (3M–DPPZ^{2+}) is positive to that of 3M–DPA to 3M–DPA$^{\bullet+}$, the 3M–DPPZ^{2+} cation is not involved in the ETSF spectroscopic measurement. This is a significant difference from the previous result of DPA$^{\bullet+}$, in which DPB$^{\bullet+}$ and DPB^{2+} are formed.[14] However, the present results can be explained similarly except for the formation of the dication. That is, the dimerization reaction proceeds *via* the reaction of two 3M–DPA$^{\bullet+}$, and after the rate-determining dimerization step, the distribution of the two states of 3M–DPPZ (*i.e.* 3M–DPPZ and 3M–DPPZ$^{\bullet+}$) can be determined by the follow-up equilibrium of eqn. (6) in solution. The increase in the spectral features observed in Figs. 4(A) and 5(A) can thus be attributed to those of 3M–DPPZ$^{\bullet+}$ and 3,3′M–DPPZ$^{\bullet+}$. In the presence of the neutral molecules, the amount of 3M–DPPZ$^{\bullet+}$ or 3,3′M–DPPZ$^{\bullet+}$ is considered to be markedly decreased reflecting the equilibrium of eqn. (6), as observed in Figs. 4(B) and 5(B). The dimerization rate constants, which are independent of the amount of neutral molecules, also verify this mechanistic conclusion.

Conclusion

While the effects of the 4-methyl substituent on the reaction routes of DPA$^{\bullet+}$ have been studied in the presence of bases previously,[9–11] the methyl substituent effects at the 3-posion were observed for the first time, as well as the detailed kinetic analysis of all the derivatives.

It is noticeable that the rate constants of 3M–DPA$^{\bullet+}$ and 3,3′M–DPA$^{\bullet+}$ were as fast as *ca.* $1.0 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$, which is faster than the dimerization of DPA$^{\bullet+}$ to form the diphenylbenzidine dimer. Although some complexity, or more required energy, would be imaginable for the formation of the DPPZ derivatives, the 3-methyl substituent has been shown to promote the reaction between the 6-position of the phenyl ring and the nitrogen molecule of another 3M–DPA$^{\bullet+}$ or 3,3′M–DPA$^{\bullet+}$. This noticeable promotion by the 3-methyl substituent can be also verified from the fact that the cyclization reaction was observed in neutral acetonitrile. Up to now, cyclization reactions have only been reported in the presence of some bases,[9–11] while the same reaction was expected in the present results for 4M–DPA$^{\bullet+}$ or 4,4′M–DPA$^{\bullet+}$ in the presence of the neutral molecules. Comparing these results, we can stress the present findings concerning the 3-methyl substituent to promote the cyclization reaction as a remarkable activation of its *para* position (*i.e.* 6-position).

As the present case represents intermolecular interaction between radical and cationic characters, knowledge of such activation of aromatic cation radicals by methyl substituents at certain positions would be important in considering the cyclization or cyclic addition reactions involving cation radicals.

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