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Transannular Distance Dependence of Stabilization Energy of the Intramolecular Dimer Radical Cation of Cyclophanes

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The intramolecular dimer radical cation and charge-transfer complex of various cyclophanes were investigated by using pulse radiolysis measurements. The charge resonance band due to the dimer radical cation of cyclophanes appeared in the near-IR region, which showed a blue-shift as the distance between the two benzene rings of cyclophane decreased. The stabilization energy of the dimer radical cation, which was estimated from the peak position of the charge resonance band, was explained by the exchange interaction, while the substituent effect was small. The absorption peak of the charge-transfer complex with chlorine atom also showed the shift in accordance with the oxidation potential of cyclophanes.

Introduction

Dimer radical cations, which are constituted of a radical cation and the parent molecule, have been investigated for years.[1−4] Dimer radical cations are important in the field of material science, because they can be regarded as the smallest units for the delocalized positive charge, which has large effects on various properties such as photoconductivity and ferromagnetism.[4,5] It is well-known that stabilization of the dimer radical cation is affected by its conformation of molecules such as distance and orientation. However, structural analysis of the dimer radical cation by X-ray crystallography is rather limited.[4] Furthermore, in solution, it is quite difficult to determine the distance between the chromophores participating in intermolecular dimer radical cation formation. Therefore, a spectroscopic study on the dimer radical cation of molecules, in which two chromophores are connected by the rigid bonds, will be beneficial to determine the factors which govern the properties of dimer radical cations.

Up to the present, various kinds of multibridged cyclophanes have been synthesized and revealed interesting properties.[6−10] A series of [3_n]cyclophanes have also been reported.[7] Among them, the synthesis of [3_6](1,2,3,4,5,6)cyclophane ([3_6]CP, Figure 1) was reported by some of the present authors and their co-workers.[7] For the multibridged cyclophanes, novel properties specific to the transannular $\pi-\pi$ interaction between the benzene rings fixed at the close proximity are expected. The unique emission properties of [3_n]cyclophanes have been reported recently.[8] Since the trimethylene bridge of [3_n]cyclophanes decreases the structural strain compared to that of [2_n]cyclophanes, [3_n]cyclophanes exhibit higher electron-donor ability. The charge-transfer complex of [3_n]cyclophanes with tetracyanoethylene exhibits significant bathochromic shift of the charge-transfer band with an increase of the number of trimethylene bridges because of enhanced transannular $\pi-\pi$ interaction and effective hyperconjugation between the benzyl hydrogen and benzene rings.[9] Therefore, the rigid structure fixed at the face-to-face conformation and the good donor ability of cyclophanes seem to be suitable to study the intramolecular dimer radical formation.

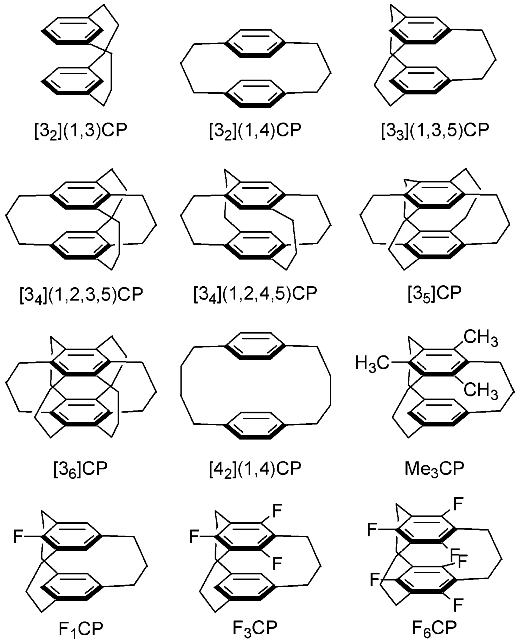

Figure 1. Molecular structures of cyclophanes.

In the previous paper, we reported formation of the intramolecular dimer radical cation of [3_3](1,3,5)cyclophane ([3_3](1,3,5)-CP), [3_5](1,2,3,4,5)cyclophane ([3_5]CP), and [3_6]CP.[10] It was revealed that the stabilization energy of the dimer radical cation depends on the transannular distance. However, the transannular distance examined therein was limited to a small range while the substitution effect was not studied. In the present investigation of the dimer radical cation, a variety of parent cyclophanes

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were included (Figure 1), which allowed us not only to investigate over a wider range of transannular distance but also to measure the effect of various substituents.

Experimental Section

Materials. Cyclophanes ([3_2](1,3)cyclophane ([3_2](1,3)CP), [3_2](1,4)cyclophane ([3_2](1,4)CP), [3_3](1,3,5)CP, [3_4](1,2,3,5)-cyclophane ([3_4](1,2,3,5)CP), [3_4](1,2,4,5)cyclophane ([3_4]-(1,2,4,5)CP), [3_5]CP, [3_6]CP, [4_2](1,4)cyclophane ([4_2](1,4)CP), 2,4,6-trimethyl-[3_3](1,3,5)cyclophane (Me_3CP), 2-fluoro-[3_3]-(1,3,5)cyclophane (F_1CP), 2,4,6-trifluoro-[3_3](1,3,5)cyclophane (F_3CP), and 2,4,6,2′,4′,6′-hexafluoro-[3_3](1,3,5)cyclophane (F_6-CP)) were synthesized according to the procedure reported previously.[7] The purity of the sample was >99% based on ^{1}-HNMR.

Apparatus. Pulse radiolysis measurement was performed with use of an electron pulse (28 MeV, 8 ns, 0.7 kGy per pulse) from a linear accelerator at Osaka University. The probe light from a 450 W Xe-lamp (Osram, XBO-450) was detected with a multichannel spectrometer (UNISOKU TSP 601-20). The kinetic traces in the visible region were measured by using a photomultiplier (Hamamatsu Photonics, R928) equipped with a monochromator (Jobin Yvon Inc., TR190MST3M). The kinetic traces and spectra in the near-IR region were measured with an InGaAs photodiode (Thorlabs Inc., PDA255). It is established that the substrates (S) were oxidized according to the following scheme in halogenated solvents (RCl) during pulse radiolysis,[11]

$$\mathrm{RCl} \rightsquigarrow \mathrm{RCl}^{\bullet+} + \mathrm{e}^-, \mathrm{RCl}^* \qquad (1)$$

$$\mathrm{e}^- + \mathrm{RCl} \rightarrow \mathrm{R}^\bullet + \mathrm{Cl}^- \qquad (2)$$

$$\mathrm{RCl}^{\bullet+} \rightarrow \mathrm{R}^+ + \mathrm{Cl}^\bullet \qquad (3)$$

$$\mathrm{RCl}^* \rightarrow \mathrm{R}^\bullet + \mathrm{Cl}^\bullet \qquad (4)$$

$$\mathrm{RCl}^{\bullet+} + \mathrm{S} \rightarrow \mathrm{S}^{\bullet+} + \mathrm{RCl} \qquad (5)$$

In the present paper, we employed 1,2-dichloroethane or dibromomethane as a solvent of pulse radiolysis experiments. The solvent used is indicated in the text. The concentration of the substrate was 1.0×10^{-2} M. Since the radical cation is generated within 10 ns, spectra of the radical cations were measured at 50 ns after the electron pulse. The sample solutions were deoxygenated by bubbling with argon for 30 min. All measurements were carried out at room temperature.

Theoretical Calculation. Optimized structures of radical cations of cyclophanes were estimated at the B3LYP/6-31Gd level with the Gaussian 03 package.[12] The optimized structures are confirmed to be the equilibrated most stable ones from the absence of imaginary frequencies.

Results and Discussion

Transannular Distance of Cyclophane Radical Cations. It is well-known that the degree of stabilization of the dimer radical cation depends on the conformation of the two chromophores participating in charge resonance. Since the conformation of the two benzene rings of the radical cation of cyclophanes is fixed in a face-to-face conformation, the distance between them should be the important parameter for the stabilization of the dimer radical cation. For some cyclophanes, crystalline structures of charge-transfer complexes, in which cyclophane bears one positive charge, have been reported.[9] Unfortunately, not all compounds investigated here have been examined in the crystallographic study of the charge-transfer complex. Thus, to evaluate the transannular distance (r) of the cyclophane radical cations, we employed the molecular orbital calculation at the B3LYP/6-31Gd level.[12] In Table 1, the distance between the two benzene rings of the cyclophane radical cations is summarized. It should be noted that the r values in Table 1 are the average of the transannular distance of the benzene carbons. The maximum and minimum distance between the two benzene rings are indicated in Table S1 in the Supporting Information.

TABLE 1: Peak Positions of the Local Excitation Band (λ_{le}), Charge Resonance Band (λ_{CR}), Stabilization Energy (E_{CR}), Transannular Distance (r), and Charge-Transfer Complex Band (λ_{CT}) of Cyclophanes

cyclophanes	λ_{le}/nm	λ_{CR}/nm	E_{CR}/kJ mol^{-1}	r/Å^a	λ_{CT}/nm^b
[3_2](1,3)CP	491	900^c	66.5	3.30	–^{e}
[3_2](1,4)CP	480	810^c	73.9	3.21	–^{e}
[3_3](1,3,5)CP	510	730	82.0	3.06	427 (–^{e})
[3_4](1,2,3,5)CP	507	710^d	84.3	3.03	458 (466)
[3_4](1,2,4,5)CP	510	730^d	81.9	3.04	455 (452)
[3_5]CP	501	696	86.0	2.96	473 (468)
[3_6]CP	519	667	89.7	2.89	486 (484)
[4_2](1,4)CP	485	1075^c	55.7	3.46	–^{e}
Me_3CP	525	760^d	78.7	3.11	465 (463)
F_1CP	520	755^d	79.2	3.06	–^{e}
F_3CP	527	780^d	76.7	3.04	–^{e}
F_6CP	532	760^d	78.7	3.04	–^{e}

[a] Estimated by DFT calculation at the B3LYP/6-31Gd level. [b] Data in parentheses are the peak positions of the charge-transfer complex generated in dibromomethane. [c] Estimation error: ±10 nm. [d] Estimation error: ±5 nm. [e] Charge-transfer band was not observed.

From the X-ray crystallographic characterization of the charge-transfer complex of cyclophanes and tetracyanoquinodimethane (TCNQ) derivatives, the r values of cyclophanes have been reported.[9] For the charge-transfer complex with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQ-F_4), the r values of radical cations of [3_3](1,3,5)CP, [3_4](1,2,3,5)-CP, [3_5]CP, and [3_6]CP have been reported to be 3.11, 3.05, 3.02, and 2.94 Å, respectively,[9] which are close to the calculated values (3.06, 3.03, 2.96, and 2.89 Å, respectively). Thus, the calculated r values for other cyclophanes will be reliable. The molecular orbital calculation evaluated the r values to be slightly shorter than those of the X-ray crystallographic characterization of the charge-transfer complex with TCNQ-F_4 by 0.02–0.06 Å. Because, in the charge-transfer complex, the charge of cyclophanes will not completely move from cyclophane to TCNQ as depicted by $CP^{\delta+}TCNQ^{\delta-}$ ($0 \leq \delta \leq 1$) (CP denotes cyclophane), the electronic repulsion between the two benzene rings of cyclophane will be slightly larger to make the r value slightly longer when compared with that in $CP^{\bullet+}$ evaluated by the molecular orbital calculation.

[4_2](1,4)CP shows the longest distance among the cyclophanes investigated because of the longest methylene bridge connecting the two benzene rings. Among the [3_n]CPs, the increase in the number of trimethylene bridges resulted in the shorter r values. In the case of Me_3CP, the r value is slightly longer than that of [3_3](1,3,5)CP, probably because of the steric effect of the methyl groups and the electronic repulsion of two benzene rings due to the electron-donating nature of the methyl groups. On the other hand, the r values of F_nCPs are slightly shorter than that of [3_3](1,3,5)CP, probably because of smaller electronic repulsion due to the electron-withdrawing nature of the F-groups.

Dimer Radical Cation Formation of Cyclophanes. Formation of the dimer radical cation of cyclophanes was examined

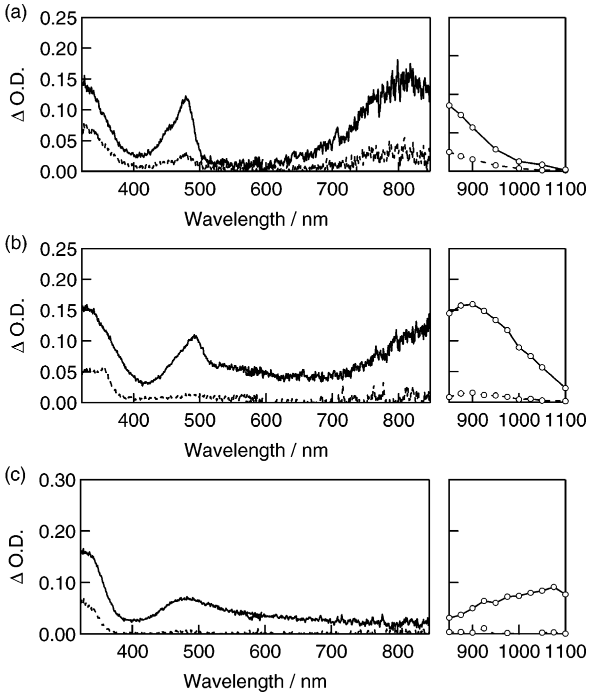

Figure 2. Transient absorption spectra observed at 50 ns (solid line) and 5 μs (broken line) after 8 ns pulse irradiation during pulse radiolysis of cyclophanes (1.0 × 10^{-2} M) ([3_2](1,4)CP (a), [3_2](1,3)CP (b), and [4_2](1,4)CP (c)) in 1,2-dichloroethane.

by pulse radiolysis measurements. Figure 2a shows the transient absorption spectra of [3_2](1,4)CP in 1,2-dichloroethane during the pulse radiolysis. The spectrum of [3_2](1,4)CP at 50 ns after the pulse irradiation exhibited sharp and broad peaks at 480 and 810 nm, respectively (Figure 2a). The absorption band at 480 nm was assigned to the local excitation band of the radical cation of [3_2](1,4)CP from the spectral similarity with the radical cation of methyl-substituted benzenes, which exhibit an absorption peak at 450−520 nm, under the condition where the dimer formation is prohibited such as in low-temperature glass.[1,11d] On the other hand, the absorption band of [3_2](1,4)CP at 810 nm can be assigned to a charge resonance band because it is well-known that a dimer radical cation generated by warming and re-freezing of low-temperature glass exhibits a charge resonance band in the near-IR region.[1,10] The observation of the charge resonance band due to the intramolecular dimer radical cation formation can reasonably be attributed to the structure of [3_2](1,4)CP, in which two benzene rings are fixed at the close proximity by the trimethylene bridges. The absorption bands due to the local excitation and charge resonance in the visible and near-IR regions, respectively, were confirmed for the other cyclophanes as listed in Table 1.

For some cyclophanes, we confirmed that the spectral shapes were independent of concentration, indicating that the intermolecular dimer formation (i.e., $CP^{\bullet+} + CP \rightarrow CP_2^{\bullet+}$) can be ruled out under the present experimental conditions.[10] Thus, it can be concluded that the present dimer radical cation formation can be attributed to the intramolecular process.

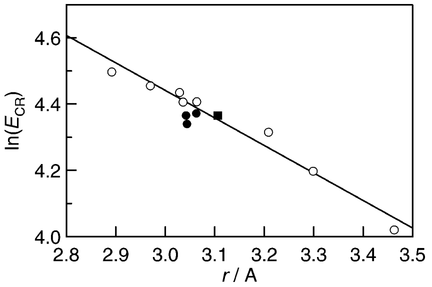

Figure 3. Distance (r) dependence on the stabilization energy (E_{CR}) for [3_n]CP and [4_2](1,4)CP (open circle), M_3CP (solid square), and F_n-CPs (solid circle). The solid line is a fitted line for [3_n]CP and [4_2](1,4)CP.

The charge resonance bands of [3_2](1,3)CP and [4_2](1,4)CP were observed at 900 and 1075 nm, respectively (Figure 2b,c), which are in a similar wavelength region as those of the intermolecular dimer radical cation of benzene derivatives. For example, the peak positions of the charge resonance bands of dimer radical cations of benzene, mesitylene, and hexamethylbenzene were reported to be 926, 1042, and 1351 nm, respectively.[1] Furthermore, charge resonance bands of the [2,2′](1,4)cyclophane and diphenylpropane were 1162 and 1250 nm, respectively.[1,11d] The observed similarity of the peak positions can be attributed to the similar transannular distance of these cyclophanes (3.2−3.5 Å) to those of intermolecular dimer radical cations of methyl-substituted benzenes as discussed in a later section.

The formation of the intramolecular dimer radical cation is also confirmed for the methyl- and fluoro-substituted cyclophanes as shown in Table 1. It should be noted that the radical cations of methyl- and fluoro-substituted cyclophanes showed the charge resonance band in as similar region as that of [3_3](1,3,5)CP, which has a similar r value to the methyl- and fluoro-substituted cyclophanes.

It is interesting to note that the width of the local excitation band of [4_2](1,4)CP is quite broad when compared with those of other cyclophanes. The full width at the half-maximum (fwhm) of the local excitation band of [4_2](1,4)CP is 4850 cm^{-1}, while those of [3_2](1,4)CP and [3_2](1,3)CP are 3220 and 2080 cm^{-1}, respectively. In addition, the fwhm of the local excitation band of [3_6]CP is 2080 cm^{-1}. Thus, the broad local excitation band of [4_2](1,4)CP can be attributed to the various conformers resulting from the tetramethylene bridges connecting the two benzene rings of [4_2](1,4)CP.

Stabilization Energy of the Dimer Radical Cation. The charge resonance band can be attributed to the transition between the states expressed as $\Phi_\pm = (1/\sqrt{2})(\varphi(M_A^+)\varphi(M_B) \pm \varphi(M_A)\varphi(M_B^+))$, where $\varphi(M_A)$ and $\varphi(M_B)$ are the wave functions of neutral molecules in the dimer radical cation and superscript "+" indicates the radical cation.[1] From the electron exchange interaction, the stabilization energy of the dimer radical cation (E_{CR}) can be expressed as $E_{CR} \propto \exp(-\beta r)$, where β is a constant.[13−15] In Table 1, the E_{CR} values, which were estimated from half energy of the charge resonance band, are also listed. In Figure 3, $\ln(E_{CR})$ was plotted against the r value calculated by the molecular orbital calculation. As shown in Figure 3, a linear relation between $\ln(E_{CR})$ and r was observed for the wide range of the r value (2.89−3.46 Å). The β value was estimated to be 0.83 Å^{-1}, using the data of [4_2](1,4)CP and [3_n]CPs. In the previous study on the dimer radical cation of [3_3](1,3,5)-CP, [3_5]CP, and [3_6]CP, we estimated the β value to be 0.51 Å^{-1},[10] which is slightly smaller than the value estimated in this study. The β value estimated in this study should be a reliable value, because the present value was estimated based on the wide range of the r value.

It is interesting to note that the E_{CR} values of Me_3CP and F_nCPs are also close to the straight line of Figure 3. This fact clearly indicates that the electron-donating or -withdrawing nature of the substituent of cyclophanes does not affect the E_{CR} values seriously. Thus, it can be concluded that the r value mainly determines the E_{CR} value of cyclophanes.

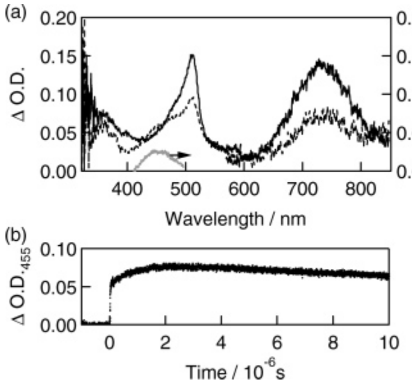

Figure 4. (a) Transient absorption spectra observed at 50 ns (solid line) and 2 μs (broken line) after 8 ns pulse irradiation during pulse radiolysis of $[3_4](1,2,4,5)$CP (1.0×10^{-2} M) in 1,2-dichloroethane. A spectrum indicated by gray was obtained by the subtraction of the spectrum at 50 ns from that at 2 μs after being normalized. (b) Kinetic trace of ΔO.D. at 455 nm during the pulse radiolysis.

Charge-Transfer Complex Formation. Figure 4a shows the transient absorption spectra of $[3_4](1,2,4,5)$CP in 1,2-dichloroethane during the pulse radiolysis. At 50 ns after the pulse irradiation, the local excitation and charge resonance bands are observed at 510 and 730 nm, respectively. On the other hand, at 2 μs after the pulse irradiation a new transient absorption band appeared around 455 nm. The new absorption band can be assigned to the charge-transfer complex of $[3_4](1,2,4,5)$CP and the chlorine atom.[16−19] This assignment was confirmed by the fact that similar charge-transfer complex bands were observed when dibromomethane was used as the solvent (Table 1). Thus, the slow generation of the charge-transfer complex in the microsecond regime (Figure 4b) is attributed to the reaction between the radical cation of cyclophane and the chloride anion (eqs 6 and 7):

$$\mathrm{CP}^{\bullet+} + \mathrm{Cl}^- \rightarrow [\mathrm{CP}^{\bullet+}\mathrm{Cl}^-] \quad (6)$$

$$\mathrm{CP}^{\bullet+} + \mathrm{Cl}^- \rightleftharpoons [\mathrm{CP}^{\bullet+}\mathrm{Cl}^-] \quad (7)$$

Formation of a charge-transfer complex by the electron transfer from substrate to chlorine atom generated from the solvent (eq 8) is also possible, although the process (eq 8) should be limited to the early stage of the pulse radiolysis, since the lifetime of the chlorine atom is reported to be 10 ns in 1,2-dichloroethane.[19]

$$\mathrm{CP} + \mathrm{Cl}^{\bullet} \rightarrow [\mathrm{CP}^{\bullet+}\mathrm{Cl}^-] \quad (8)$$

As seen in the spectrum of $[3_4](1,2,4,5)$CP at 2 μs after the pulse irradiation, the local excitation and charge resonance bands remained even after formation of the charge-transfer complex. The formation of the charge-transfer complex is plausibly an equilibrium with the radical cation for $[3_4](1,2,4,5)$CP (eq 7) as in the cases of $[3_5]$CP and $[3_6]$CP, while the formation of the charge-transfer complex by eq 6 was observed for $[3_3]$-(1,3,5)CP, probably due to the substantial charge shift on the formation of the charge-transfer complex $[[3_3](1,3,5)\mathrm{CP}^{\bullet+}\mathrm{Cl}^-]$, which shows the largest spectral shift on the formation of the charge-transfer complex.[10]

The formation of the charge-transfer complex according to eq 7 was also indicated for $[3_4](1,2,3,5)$CP and $\mathrm{Me_3CP}$ because these cyclophanes showed generation of the band with similar reaction kinetics. The peak positions of the charge-transfer bands, which were estimated by subtraction of the spectral contribution of the radical cation, are also listed in Table 1. On the other hand, $[4_2]$CP, $[3_2](1,3)$CP, $[3_2](1,4)$CP, and F_nCPs did not show the absorption band attributable to the charge-transfer complex, probably because of the lower electron donor-ability of these cyclophanes.

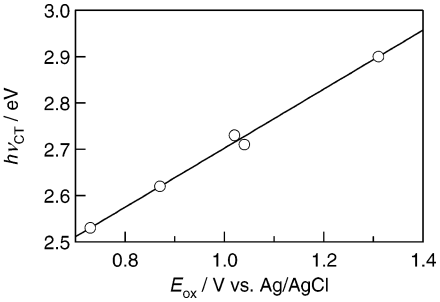

Figure 5. Oxidation potential (E_{ox}) dependence on the peak position of the charge-transfer complex ($h\nu_{CT}$).

It became clear that the peak position of the charge-transfer band shifted to the longer wavelength side as the number of trimethylene bridges increases. It is well established that the absorption band of the charge-transfer complex of the halogen atom and the aromatic molecule shifts to the longer wavelength side as the donor-ability increases.[17] In the case of the present $[3_n]$cyclophanes, the oxidation potentials (E_{ox}) have been reported to be 1.31, 1.04, 1.02, 0.87, and 0.73 V vs Ag/AgCl for $[3_3](1,3,5)$CP, $[3_4](1,2,3,5)$CP, $[3_4](1,2,4,5)$CP, $[3_5]$CP, and $[3_6]$CP, respectively.[9] The linear relation between the E_{ox} and the peak position of the charge-transfer band ($h\nu_{CT}$) was confirmed as shown in Figure 5. Thus, it can reasonably be concluded that the peak shift is caused by the stabilization of the charge-transfer complex.

The peak position of the charge-transfer complex of $\mathrm{Me_3CP}$ is an intermediate of $[3_4]$CPs and $[3_5]$CP. The observed peak position seems to be reasonable when taking the number of methyl substituents into consideration, i.e., the number of methyl or methylene substituents is 8, 9, and 10 for $[3_4]$CPs, $\mathrm{Me_3CP}$, and $[3_5]$CP, respectively.

Conclusion

In the present study, we reported spectroscopic properties of dimer radical cations of a variety of cyclophanes using the pulse radiolysis measurements. It was revealed that the stabilization energy of the dimer radical cation, which can be estimated from the peak position of the charge resonance band, largely depends on the distance between the two benzene rings of cyclophanes. The effect of electron-donating or -withdrawing nature of the substituent on the stabilization energy was rather small compared with the effect of the transannular distance. Formation of the charge-transfer complex with the chlorine atom was also confirmed. The peak position of the charge-transfer complex shows a good relation with the oxidation potentials.

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Supporting Information Available: Optimized structures of radical cations of $[3_6]$CP and $[3_2](1,3)$CP and averaged, minimum, and maximum distances between two benzene rings of the radical cation and neutral cyclophanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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