J. Phys. Chem. A **2005,** *109,* 3531−3534

ARTICLES

Formation of Highly Stabilized Intramolecular Dimer Radical Cation and π-Complex of $[3_n]$Cyclophanes ($n = 3, 5, 6$) during Pulse Radiolysis

Mamoru Fujitsuka,[†] Shingo Samori,[†] Michihiro Hara,[†] Sachiko Tojo,[†] Satoko Yamashiro,[‡] Teruo Shinmyozu,[‡] and Tetsuro Majima*,[†]

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan, and Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581, Japan

Received: January 23, 2005; In Final Form: March 2, 2005

Formation of radical cation and charge-transfer complex of $[3_n]$cyclophanes ($n = 3, 5, 6$) was investigated by transient absorption spectroscopy during pulse radiolysis. Radical cations of $[3_n]$cyclophanes showed the charge resonance band around 700 nm which exhibited a blue-shift as the number of trimethylene bridges increased, indicating formation of highly stabilized intramolecular dimer radical cation of $[3_n]$cyclophanes. The absorption peak of the charge-transfer complex with chlorine atom also showed the shift in accord with the oxidation potential of $[3_n]$cyclophanes.

Introduction

Up to the present, various kinds of multibridged cyclophanes have been synthesized and have revealed interesting properties.[1] A series of $[3_n]$cyclophanes have also been reported.[2−5] 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.[2,3] 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.[5] Since the trimethylene bridge of $[3_n]$cyclophanes decreases the structural strain compared to $[2_n]$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 hyper conjugation between the benzyl hydrogen and benzene rings.[4]

Despite these studies on the charge-transfer complex, spectral features of the radical cations of $[3_n]$cyclophanes have not been reported. Especially, the stabilization of the charged state by the transannular interaction is an interesting subject. Since the benzene rings in the $[3_n]$cyclophanes are held at the fixed distance, spectral feature of $[3_n]$cyclophanes will give critical aspects. Herein, we report the transient absorption spectra of radical cations of $[3_3]$(1,3,5)cyclophane ($[3_3]$CP), $[3_5]$(1,2,3,4,5)-cyclophane ($[3_5]$CP), and $[3_6]$CP (Figure 1). For generation of the radical cation, we employed pulse radiolysis, because radiolysis generates a strong oxidant capable of oxidizing various organic compounds.[6] In the haloalkane solvents employed, subsequently the charge-transfer complex formation with chlorine atom was also observed. Their spectral features are discussed on the structural basis. The observed properties of $[3_n]$cyclophanes will be an excellent example of how precise control over chromophores in supramolecular structure can be used to tune spectroscopic properties in ways that could be exploited in nanoscale devices.

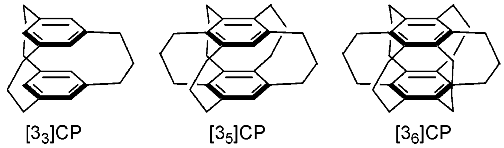


Figure 1. Molecular structures of $[3_n]$cyclophanes ($n = 3, 5, 6$).

Experimental Section

Materials. $[3_n]$cyclophanes were synthesized according to the procedure reported previously.[2−5] The purity of the sample was >99% on the basis of ^{1}HNMR.

Apparatus. Pulse radiolysis was performed using 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 were estimated using a photomultiplier equipped with a monochromator (CVI-Laser, Digikrom-240). It is established that the substrates (S) were oxidized according to the following scheme in halogenated solvents (RCl)[6]

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

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

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

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

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

---

* Author to whom correspondence should be addressed. E-mail: majima@sanken.osaka-u.ac.jp.
[†] Osaka University.
[‡] Kyushu University.

10.1021/jp050397z CCC: $30.25

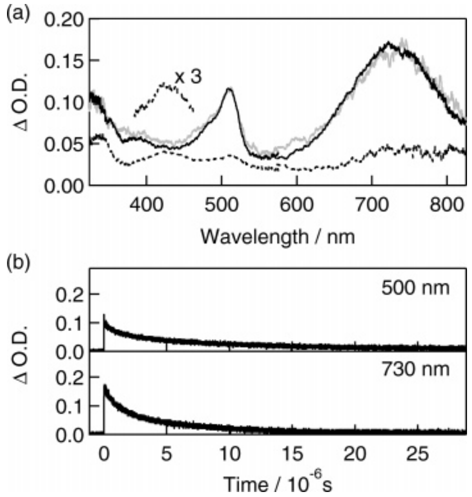


Figure 2. (a) Transient absorption spectra of $[3_3]$CP (1.0×10^{-2} M) in 1,2-dichloroethane at 50 ns (solid line) and 5 μs (broken line) after 8-ns pulse irradiation during pulse radiolysis. Spectrum indicated by gray was measured at 50 ns after the pulse during the pulse radiolysis of $[3_3]$CP (2.0×10^{-3} M). Spectrum is normalized. (b) Kinetic traces of ΔO.D. at 500 and 730 nm.

In the present paper, we employed 1,2-dichloroethane as a solvent for pulse radiolysis. Concentration of the substrate was 1.0×10^{-2} M. Because of poor solubility of $[3_6]$CP in 1,2-dichloroethane, dichloromethane was used as a solvent for $[3_6]$CP, of which concentration was $<2.0 \times 10^{-3}$ M. The sample solutions were deoxygenated by bubbling with argon for 30 min. All measurements were carried out at room temperature.

Results and Discussion

Figure 2 a shows the transient absorption spectra of $[3_3]$CP in 1,2-dichloroethane during pulse radiolysis. The spectrum of $[3_3]$CP at 50 ns after the pulse irradiation exhibited the sharp and broad peaks at 510 and 730 nm, respectively. The absorption band at 510 nm was assigned to the local excitation band of radical cation of $[3_3]$CP from the spectral similarity with the radical cation of mesitylene under the condition where the dimer formation is prohibited such as in low-temperature glass.[7] On the other hand, the absorption band of $[3_3]$CP at 730 nm can be assigned to a charge resonance band because it is well-known that dimer radical cation generated by warming and refreezing of low-temperature glass exhibits a charge resonance band in near-IR region.[7,8] The observation of the charge resonance band due to the intramolecular dimer radical cation formation can reasonably be attributed to the structure of $[3_3]$CP, in which two benzene rings are fixed at the close proximity. Similarly, $[3_5]$CP and $[3_6]$CP radical cations revealed their respective local excitation bands at 501 and 519 nm, while their charge resonance bands appeared at 696 and 667 nm, respectively (Figures 3 and 4).

The transient absorption spectra of $[3_3]$CP and $[3_5]$CP were also measured by reducing concentration of the substrates to 2.0×10^{-3} M. As shown in Figures 2 and 3, the spectral shapes were independent of concentration, indicating that the intermolecular dimer formation (i.e., $[3_n]\mathrm{CP}^{\bullet+} + [3_n]\mathrm{CP} \rightarrow ([3_n]\mathrm{CP})_2{}^{\bullet+}$) can be ruled out under the present experimental conditions. As for $[3_6]$CP, intermolecular dimer formation is also assumed to be negligible because of its lower solubility. Thus, the dimer radical cation observed in Figures 2−4 can be attributed solely to the intramolecular dimer radical cation.

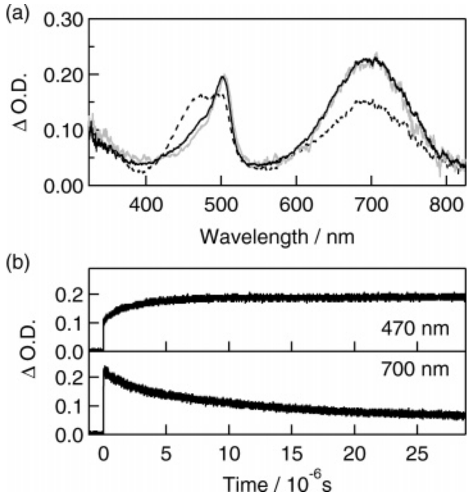


Figure 3. (a) Transient absorption spectra of $[3_5]$CP (1.0×10^{-2} M) in 1,2-dichloroethane at 50 ns (solid line) and 5 μs (broken line) after 8-ns pulse irradiation during pulse radiolysis. Spectrum indicated by gray was measured at 50 ns after the pulse during the pulse radiolysis of $[3_5]$CP (2.0×10^{-3} M). Spectrum is normalized. (b) Kinetic traces of ΔO.D. at 470 and 700 nm.

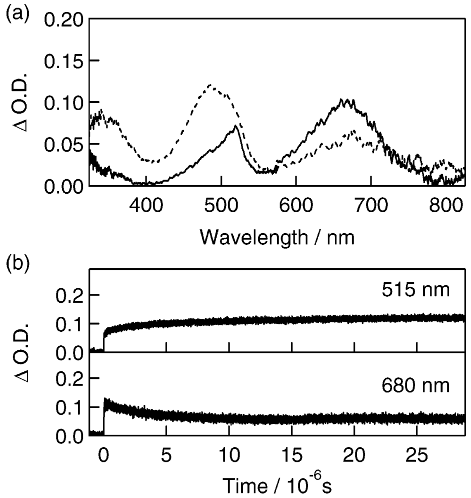


Figure 4. (a) Transient absorption spectra of $[3_6]$CP ($<2 \times 10^{-3}$ M) in dichloromethane at 50 ns (solid line) and 5 μs (broken line) after 8-ns pulse irradiation during pulse radiolysis. (b) Kinetic traces of ΔO.D. at 515 and 680 nm.

It should be stressed that the absorption peaks of the charge resonance bands appeared at shorter wavelength compared to those reported for the 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.[7] Furthermore, charge resonance bands of the [2,2′](1,4)cyclophane and diphenylpropane were 1162 and 1250 nm, respectively.[7] The stabilization energies (E_{CR})[9] of intramolecular dimer radical cations of $[3_3]$CP, $[3_5]$CP, and $[3_6]$CP were estimated to be 82.0, 86.0, and 89.7 kJ mol^{-1}, respectively, which are larger than those of the abovementioned dimer radical cations of benzene derivatives by 17.3−45.4 kJ mol^{-1}, indicating that the $[3_n]$cyclophanes form the highly stabilized intramolecular dimer radical cations.

It has been reported for aromatic hydrocarbons in low-temperature glass that an increase of the molecular size decreases E_{CR} because the electronic repulsion increases the equilibrium distance between the molecules.[10] Furthermore, the most stable structure of intramolecular dimer radical cation of dinaphthylpropane is not the conformation that gives “total overlap” of the π-electron systems because of the electronic repulsion.[11] In

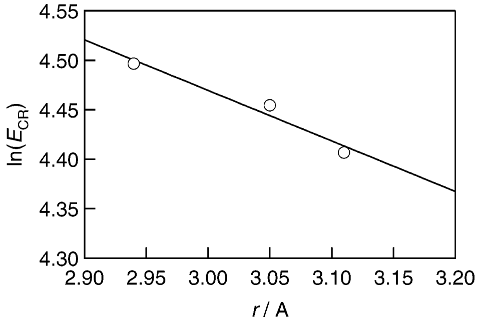
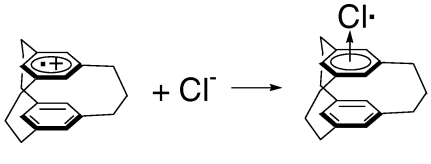


Figure 5. Distance (r) dependence on the stabilization energy (E_{CR}).

the present [3_n]cyclophanes, two benzene rings are fixed at the conformation in which the total overlap configuration is the only possible structure. Thus, the interaction between the two benzene rings plays an important role in the stabilization of the dimer radical cation. The distance between the two benzene rings of [3_3]CP, [3_5]CP, and [3_6]CP in the charge-transfer complex with tetracyanoquinodimethane (TCNQ) derivatives were reported to be 3.11−3.12, 2.94−3.02, and 2.94 Å, respectively,[4] which is shorter than the distance supposed for the cofacial stacks of the aromatic rings (3.2−3.5 Å).[12] Furthermore, the E_{CR} value of [3_n]cyclophanes became larger as the distance between the two benzene rings decreased. Therefore, it can be concluded that shorter interannular distance of [3_n]cyclophanes stabilizes the intramolecular 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.[7,8] From the electron-exchange interaction, the E_{CR} value can be expressed as $E_{CR} \propto \exp(-\beta r)$, where β and r are a constant and distance between the benzene rings, respectively.[13−15] In Figure 5, ln(E_{CR}) was plotted against r value reported for the 1:1 charge-transfer complex of [3_n]cyclophanes and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQ-F_4).[4,16] As shown in Figure 5, a plausibly linear relation was observed between ln(E_{CR}) and r. The β value was estimated to be 0.51 $Å^{-1}$. By applying the estimated relation between ln(E_{CR}) and r to the dimer radical cations of benzene and mesitylene, interannular distances were evaluated to be 3.59 and 3.82 Å, respectively, which agreed well with the values expected for the intermolecular dimer radical cations, indicating that the formation of highly stabilized dimer radical cation of [3_n]cyclophanes is attributable to the shorter distance between the two benzene rings.

At 5 μs after the pulse irradiation, a new transient absorption band appeared around 430−490 nm as seen in Figures 2a, 3a, and 4a. The absorption band can be assigned to the charge-transfer complex of [3_n]cyclophane and chlorine atom.[17−20] Since the similar absorption band was also observed when carbon tetrachloride was used as a solvent, the contribution of haloalkyl radicals such as $C_2H_4Cl^{\bullet}$ can be ruled out from the origin of the 430−490 nm band. Thus, the slow generation of the charge-transfer complex in the microsecond regime (Figures 2b, 3b, and 4b) is attributed to the following reaction:



(6)

Formation of the charge-transfer complex in the early stage of the radiolysis can be attributed to the electron transfer from the substrate to the chlorine atom generated from the solvent. Thus, the slow generation of the charge-transfer complex in the microsecond regime (Figures 2b, 3b, and 4b) can be attributed to the collisional process between the radical cation and the chloride ion.[20]

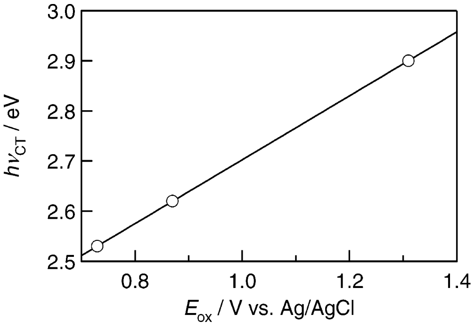
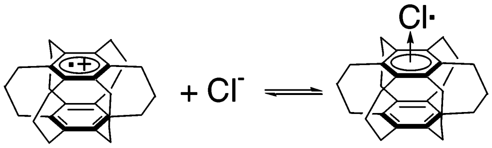


Figure 6. Oxidation potential (E_{ox}) dependence on the peak position of the charge-transfer complex ($h\nu_{CT}$).

The difference of the absorption peaks accompanying the complex formation was estimated to be 0.47, 0.14, and 0.16 eV for [3_3]CP, [3_5]CP, and [3_6]CP, respectively, indicating substantial charge shift in [3_3]CP. As seen in the spectra of [3_5]CP and [3_6]CP (Figures 3a and 4a), the absorption bands due to local excitation and charge resonance remained even after formation of the charge-transfer complex, while local excitation and charge resonance bands disappeared after charge-transfer complex formation in [3_3]CP (Figure 2a). In [3_5]CP and [3_6]CP, absorption bands due to local excitation, charge resonance, and charge-transfer complex decayed over several hundred microseconds. From these findings, the formation of the charge-transfer complex is plausibly an equilibrium with the radical cation for [3_5]CP and [3_6]CP (eq 7):



(7)

The peak position of the charge-transfer band shifted to the longer wavelength side as the number of trimethylene bridges increased (427, 473, and 486 nm for [3_3]CP, [3_5]CP, and [3_6]CP, respectively). 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.[18] In the present [3_n]cyclophanes, the oxidation potentials (E_{ox}) were reported to be 1.31, 0.87, and 0.73 V versus Ag/AgCl for [3_3]CP, [3_5]CP, and [3_6]CP, respectively.[4] 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 6. Thus, it can reasonably be concluded that the peak shift is caused by the stabilization of the charge-transfer complex.

Conclusions

We reported that the radical cations of [3_n]cyclophanes showed a charge resonance band which indicates the high stabilization of the intramolecular dimer radical cation as the number of the trimethylene bridges increased. The significant stabilization can be attributed to the shorter distance between the two benzene rings. Formation of the charge-transfer complex with the chlorine atom was also confirmed.

Acknowledgment. We thank the members of the Radiation Laboratory of ISIR, Osaka University for running the linear accelerator. This work has been partly supported by a Grant-in-Aid for Scientific Research on Priority Area (417) and others from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japanese Government.

References and Notes

(1) Vögtle, F. *Cyclophan-Chemie*; B. G. Teubner: Stuttgart, Germany, 1990.

(2) Sakamoto, Y.; Miyoshi, N.; Shinmyozu, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 549.

(3) Sakamoto, Y.; Miyoshi, N.; Hirakida, M.; Kusumoto, S.; Kawase, H.; Rudzinski, J. M.; Shinmyozu, T. *J. Am. Chem. Soc.* **1996**, *118*, 12267.

(4) Yasutake, M.; Koga, T.; Sakamoto, Y.; Komatsu, S.; Zhou, M.; Sato, K.; Tatemitsu, H.; Onaka, S.; Aso, Y.; Inoue, S.; Shinmyozu, T. *J. Am. Chem. Soc.* **2002**, *124*, 10136.

(5) Nogita, R.; Matohara, K.; Yamaji, M.; Oda, T.; Sakamoto, Y.; Kumagai, T.; Lim, C.; Yasutake, M.; Shimo, T.; Jefford, C. W.; Shinmyozu, T. *J. Am. Chem. Soc.* **2004**, *126*, 13732.

(6) (a)Arai, S.; Ueda, H.; Firestone, R. F.; Dorfman, L. M. *J. Chem. Phys.* **1969**, *50*, 1072. (b) Shank, N. E.; Dorfman, L. E. *J. Chem. Phys.* **1970**, *52*, 4441. (c) Hamil, W. H. In *Radical Ions*; Kaiser, E. T., Kevan, L., Eds.; Wiley: New York, 1968; p 321. (d) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(7) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2582.

(8) Badger, B.; Brocklehurst, B. *Nature (London)* **1968**, *219*, 263.

(9) The stabilization energy (E_{CR}) of the dimer radical cation was estimated from the half energy of the charge resonance band.

(10) Kira, A.; Imamura, M. *J. Phys. Chem.* **1979**, *83*, 2267.

(11) Tsuchida, A.; Tsujii, Y.; Ito, S.; Yamamoto, M.; Wada, Y. *J. Phys. Chem.* **1989**, *93*, 1244.

(12) Kochi, J. K.; Rathore, R.; Le Maguères, P. *J. Org. Chem.* **2000**, *65*, 6826.

(13) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(14) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.

(15) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(16) In Figure 5, r values of the charge-transfer complex of [3_n]-cyclophanes and TCNQ-F_4 were employed because a series of r values of 1:1 complex were reported only for TCNQ-F_4 (ref 4).

(17) Bühler, R. E.; Ebert, M. *Nature (London)* **1967**, *214*, 1220.

(18) Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1989**, *93*, 564.

(19) Sumiyoshi, R.; Kawasaki, M.; Katayama, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2510.

(20) Ichinose, N.; Majima, T. *Chem. Phys. Lett.* **2000**, *322*, 15.