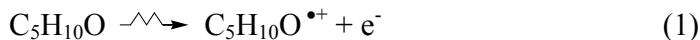


# Intramolecular dimer radical anion of [3<sub>n</sub>]cyclophanes: transannular distance dependent stabilization energy

Mamoru Fujitsuka,<sup>†</sup> Sachiko Tojo,<sup>†</sup> Teruo Shinmyozu,<sup>‡</sup> and Tetsuro Majima<sup>†\*</sup>

## Details of $\gamma$ -ray radiolysis

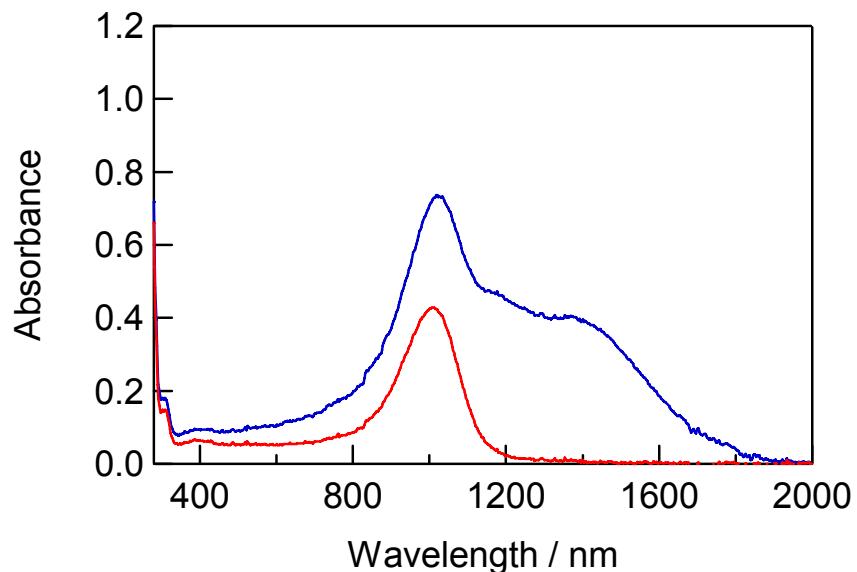
In the present study, the radical anion of cyclophane was generated by  $\gamma$ -ray radiolysis. It is established that solute (S) in MTHF (C<sub>5</sub>H<sub>10</sub>O) glassy matrix at 77 K is reduced according to the following reactions,<sup>1</sup>



When the electron generated in (1) was trapped by matrix, which shows absorption in the near-IR region, photoirradiation (> 700 nm) was carried out in order to enhance reaction (3).

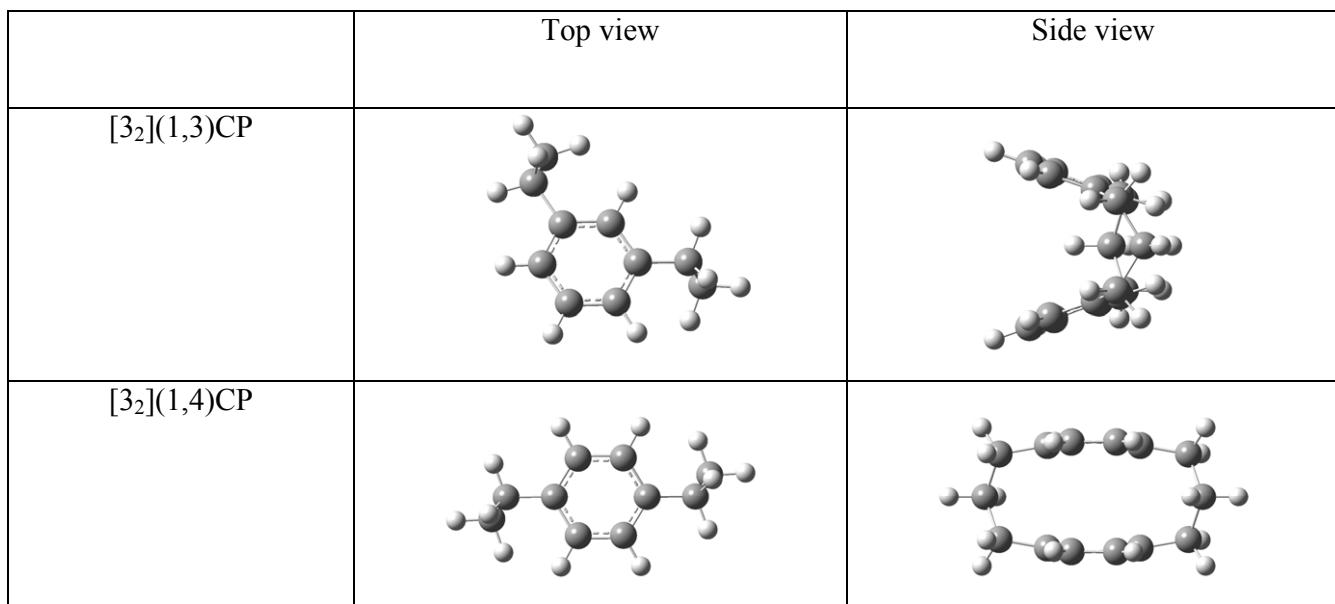
In the present experiment, sample was prepared in a Suprasil cell with a 1 or 2 mm of optical path length. After the freeze-pump-thaw cycle, the degassed sample was plunged into liquid nitrogen to form transparent glassy matrix, to which  $\gamma$ -ray from <sup>60</sup>Co source of was irradiated at the Radiation Laboratory of ISIR, Osaka University. Absorption spectra were recorded using Shimadzu UV-3100PC.

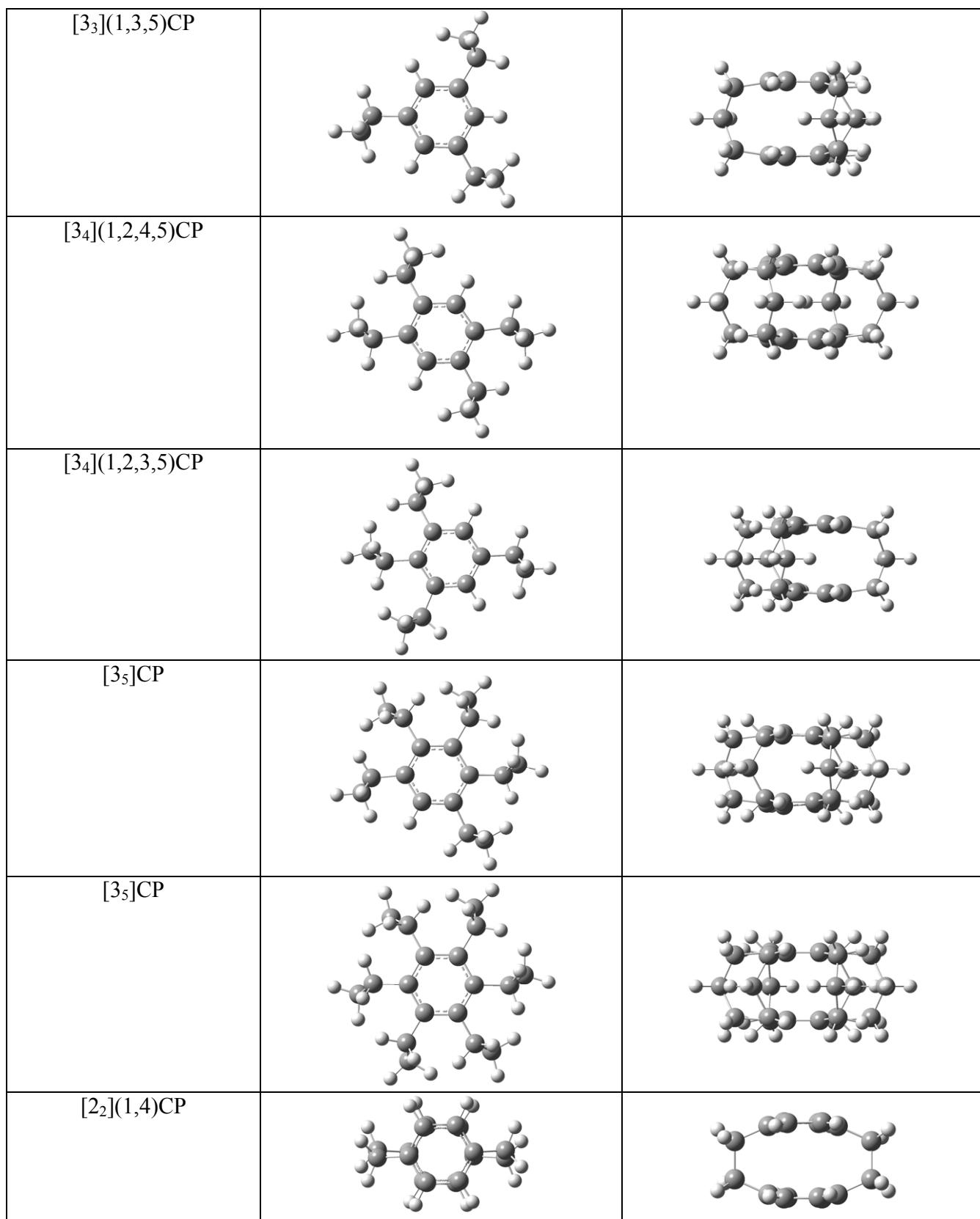
**Absorption spectra of  $[3_3](1,3,5)$ CP after  $\gamma$ -radiolysis.**



**Figure S1.** Absorption spectra of  $[3_3](1,3,5)$ CP in MTHF glassy matrix at 77 K after  $\gamma$ -radiolysis. Blue line is after  $\gamma$ -radiolysis. Red line is after photoirradiation.

**Energy-minimized structures of radical anion of cyclophane.**





**Figure S2.** Energy-minimized structures of radical anion of cyclophanes calculated at UB3LYP/6-31+G(d) level. Top and side views.

### Full citation for reference 22

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

### Reference

- 1 T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988.