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

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Transannular distance of cyclophanes. In Figure S1, optimized structures of radical cations of $[3_6]$CP and $[3_2](1,3)$CP were indicated as representatives. In the case of $[3_6]$CP, two benzene rings are coplanar and stacked completely. In the case of the cyclophanes with lower symmetry, two benzene rings are also stacked but slightly deviated from complete coplanar structure as indicated in Table S1. In the case of $[3_2](1,3)$CP, deviation from the coplanar structure is confirmed by eyes as seen in the side view of Figure S1, although the stacked structure is maintained.

In Table S1, transannular distances of neutral cyclophanes are also indicated. The transannular distance of neutral radical cation is larger than that of corresponding radical cation by 0.10 - 0.14 Å except for $[3_2](1,3)$CP and $[4_2](1,4)$CP. The larger distance of neutral cyclophanes can be attributed to the electronic repulsion. In the case of $[3_2](1,3)$CP and $[4_2](1,4)$CP, differences in the distance are 0.40 and 0.43 Å, respectively. The larger distance change can be attributed to the flexible structures of these cyclophanes.
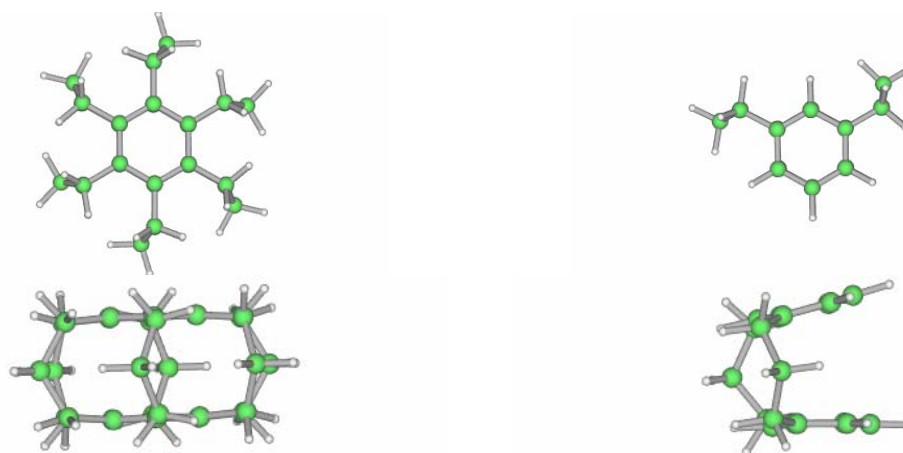
Figure S1. Top (upper panel) and side (lower panel) views of radical cation of $[3_6]$CP (right) and $[3_2](1,3)$CP (left).

TABLE S1: Averaged (r), Minimum (r_{min}), and Maximum (r_{max}) Distances Between Two Benzene Rings of Radical Cation and Neutral Cyclophanes [a]

Cyclophanes	Radical cation			Neutral		
	r / Å	r_{min} / Å	r_{max} / Å	r / Å	r_{min} / Å	r_{max} / Å
$[3_2](1,3)$CP	3.30	3.06	3.69	3.73	3.04	4.53
$[3_2](1,4)$CP	3.21	3.08	3.27	3.35	3.23	3.42
$[3_3](1,3,5)$CP	3.06	3.00	3.12	3.20	3.17	3.22
$[3_4](1,2,3,5)$CP	3.03	2.84	3.18	3.13	3.00	3.21
$[3_4](1,2,4,5)$CP	3.04	2.97	3.16	3.15	3.09	3.22
$[3_5]$CP	2.96	2.86	3.20	3.07	2.98	3.27
$[3_6]$CP	2.89	2.89	2.89	2.99	2.99	2.99
$[4_2](1,4)$CP	3.46	3.20	3.65	3.86	3.59	4.14
Me_3CP	3.11	3.06	3.17	3.21	3.17	3.25
F_1CP	3.06	3.01	3.13	3.18	3.15	3.22
F_3CP	3.04	3.01	3.08	3.18	3.14	3.21
F_6CP	3.04	3.01	3.08	3.16	3.14	3.20

[a] Estimated by DFT calculation at B3LYP/6-31Gd level.