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An Alternative Synthetic Route of [3₅](1,2,3,4,5)Cyclophane, and Structural Properties of Multibridged [3ₙ]Cyclophanes and Their Charge-Transfer Complexes in the Solid State[1]

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Abstract: To develop an improved synthetic route to [3₆](1,2,3,4,5,6)cyclophane (CP) **2**, a more practical synthetic route to [3₅](1,2,3,4,5)CP **3** than the original one was developed, which started from [3₂](1,3)CP **7** via [3₄](1,2,4,5)CP **5**. The fundamental structural parameters of [3ₙ]CPs ($n = 3-6$) in the solid state were elucidated, and the observed structures were in good agreement with the most stable conformers in solution and those predicted by the theoretical calculations. In the case of [3₆]CP **2**, the most stable C_{6h} structure was observed in the crystal structure of the **2**-TCNQ-F₄ (1:1) complex, whereas the highly strained structure with a D_{6h} symmetry was observed in the crystal structure of **2** and the **2**:TCNQ:benzene (1:1:1) complex because of a severe disorder problem. [3ₙ]CPs ($n > 3$) showed reversible redox processes, and **2** (+0.39 V vs F_c/F_c^+, Cl₂CHCHCl₂) showed the lowest first half-wave oxidation potential [$E_{1/2}$ (I)] in [3ₙ]CPs. The $E_{1/2}$ (I) data support the strong donating ability of **2** and its lower homologues. This is attributed to their molecular structures where effective hyperconjugation between the benzyl hydrogens and benzene ring is possible. By taking advantage of the strong electron-donating ability of [3ₙ]CPs, their CT complexes with TCNE, TCNQ, and TCNQ-F₄ were prepared, and their crystal structural properties were examined. The single-crystal conductivity data of the CT complexes indicated that the TCNQ-F₄ complexes showed higher conductivities than the corresponding TCNQ complexes mainly due to a larger charge separation. Among the [3ₙ]CP-TCNQ complexes, the [3₃](1,3,5)CP **6**-TCNQ-F₄ (1:1) complex showed the highest conductivity (10^{-4} S cm⁻¹), and this was ascribed to the formation of an infinite column of partially overlapped acceptors with a short acceptor–acceptor distance, while the formation of such a column was not observed in the **2**-TCNQ-F₄ complex. Although the conductivities of the cyclophane-CT complexes are much lower than those of the TTF related complexes, this study successfully provides the basic knowledge for understanding the CT interactions in the solid state.

1. Introduction

The term multiple-bridged cyclophane[3] is understood to denote those with more than two bridges. The first ones are the [2ₙ]cyclophanes ([2ₙ]CPs), which contain three to six ethano bridges and two benzene rings. The synthesis of [2₆](1,2,3,4,5,6)-CP **1** (superphane) was independently accomplished by Boekel-

heide et al.[4] and Hopf et al.,[5] and the chemistry of multibridged [2ₙ]CPs has been studied in detail by them.[6,7] The next higher homologues, multibridged [3ₙ]CPs, are also available because of our efforts aimed at the synthesis of [3₆](1,2,3,4,5,6)CP **2**, which looks like a pinwheel with six blades.[8] Elongation of the bridges produced the cyclophane structure more strain-free and

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(1) Multibridged [3ₙ]cyclophanes, part 13. This paper is taken in part from the Ph.D. Dissertation of M. Yasutake of Kyushu University.[2]
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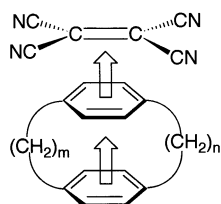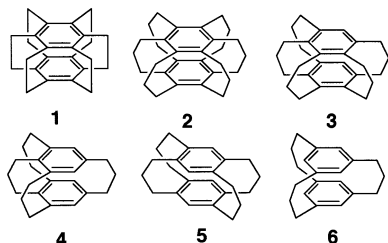
Figure 1. Charge-transfer complex between [*m.n*]paracyclophane (*m* = *n* = 2−6) and TCNE.

flexible than the corresponding [2n]CPs. As a result, the [3n]-CPs show a much stronger electron-donating ability than the corresponding [2n]CPs and interesting conformational isomerism in solution.[8−12]

Cram et al. first revealed that cyclophane serves as a good electron donor and forms CT complexes with electron acceptors as represented by tetracyanoethylene (TCNE) and the CT interaction is dependent on the chain length, and the [3.3]system shows the strongest interaction for a series of TCNE-[*m.n*]para-cyclophane complexes (*m* = *n* = 2−6) (Figure 1).[13] Since then, cyclophanes have served as excellent model compounds for the study of CT interactions.[7] In the CT absorption bands of TCNE-[2n]-[4b,14] and [3n]CPs,[8b] the band gradually shifts to a longer wavelength region with an increase in the number of bridges ranging from 594 nm for [33](1,3,5)CP **6** to 728 nm for **2**, whereas the band shifts very slightly to the longer wavelength region from 559 nm for [23](1,3,5)CP to 572 nm for [26]CP **1** with an increase in the number of bridges. The value of 728 nm for the TCNE-**2** complex is the longest wavelength among those of the TCNE-[*m.n*]CPs and other cyclophanes.[8b] Thus, the [3n]CPs have a much stronger donating ability than the corresponding [2n]CPs.

We have already studied the synthesis of the [3n]CPs and their structural properties in solution, but several important subjects still remain to be examined: (1) solid-state structural properties of [3n]CPs, (2) a study on the electrical and structural properties of the CT complexes of [3n]CPs as electron donors with electron acceptors such as TCNQ for the development of new electron-conducting materials, (3) development of improved

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Scheme 1. Two Synthetic Routes to [36]CP **2** Starting from [33](1,3,5)CP **6** or [32](1,3)CP **7** via [34](1,2,4,5)CP **5**

synthetic routes to [36]CP **2**, and (4) synthesis of propella[3n]-prismanes via photochemical reactions of [3n]CPs.[15,16] First, we studied an improved synthetic route of [35]CP **3** as a synthetic precursor to **2**. We then examined the solid-state structural properties of [3n]CPs and their CT complexes with TCNQ and TCNQ-F4. [36]CP **2** is a very strong donor as is shown by its oxidation potential ($E_{1/2}$ (I), +0.39 V (vs F_c/F_c^+)); therefore, the [3n]CPs may be promising candidates for new electron donors for the development of new electron-conducting materials. We describe here an improved synthetic route of **3**, the structural properties of [3n]CPs in the solid state, and the electrical and structural properties of the CT complexes of [3n]-CPs with acceptors such as TCNE, TCNQ, and TCNQ-F4.

The CT interactions between [22]CPs and TCNQ or TCNE in solution were studied by Mourad et al.[17] However, only a limited number of papers on the solid-state structural study of the CT complexes of the cyclophanes have been reported. Trueblood et al. reported the crystal structure of the 1:1 complex of [32](1,4)CP with TCNE.[18] Renault et al. studied the $\pi-\pi$ stacking geometries of the TCNE-cyclophane complexes ([23]- and [24](1,4)CPs,[19a,b] [22](1,4)CP,[19b] and [22](1,3)(1,4)CP[19c]) using an X-ray structural analysis and theoretical calculations.[19d,e]

2. Results and Discussion

2.1. An Alternative Synthetic Route of [35](1,2,3,4,5)-Cyclophane. [36]CP **2** was previously synthesized via the stepwise introduction of an additional trimethylene bridge into a cyclophane starting from [33](1,3,5)CP **6** (Scheme 1).[8] The intramolecular aldol condensation between an acetyl group and a pseudogeminally substituted formyl group is a key reaction. This reaction proceeds in very high yield, and the resulting enones can be readily reduced to give trimethylene bridges. Part of the original route of **2** is shown in Scheme 2 as a reference. According to this route, **2** was synthesized in 16 steps from **6** with an overall yield of 3.8%.[8a,b] The crystal structure of an important synthetic intermediate of the aldol reaction, *pseudo-*

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Scheme 2. Original Synthetic Route to [3₆]CP **2** from [3₄](1,2,3,5)CP **4**
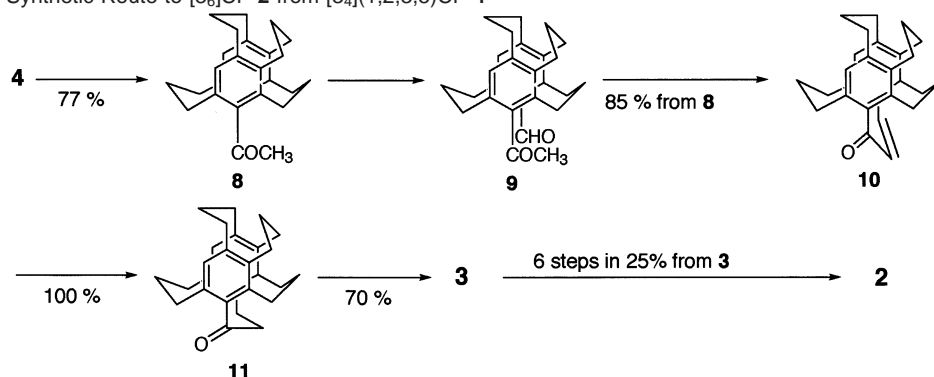
Scheme 3. Improved Synthetic Route to [3₆]CP **2** from [3₂](1,3)CP **7** via [3₄](1,2,4,5)CP **5**[a]
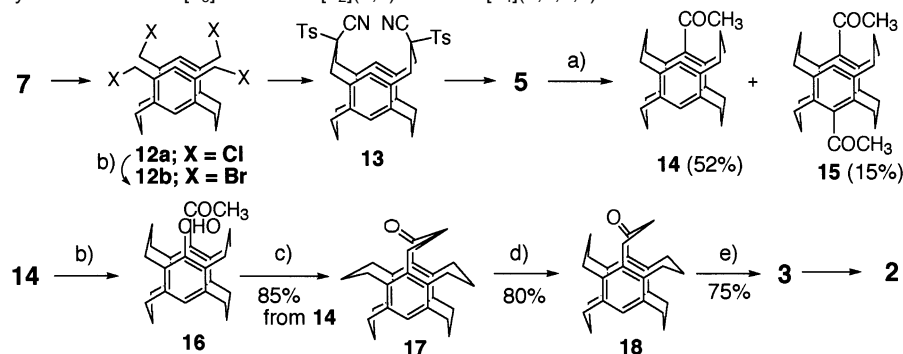
[a] (a) (CH₃CO)₂O, AlCl₃, CS₂; (b) CH₃OCHCl₂, AlCl₃, CH₂Cl₂; (c) 3 N aqueous NaOH, THF, CH₃OH; (d) H₂, 10% Pd/C, THF−CH₃OH; (e) AlCl₃, LiAlH₄, THF.

gem-acetylformyl[3₄](1,2,3,5)CP **9**, was determined. The acetyl group is perpendicular to the attached benzene ring, and the carbonyl oxygen is directed toward the inside of the molecule, whereas the formyl group is located in the plane of the attached benzene ring. These structural properties clearly explain the chemical reactivity of **9**. The acetyl group does not deactivate the attached benzene ring, and this allows the introduction of a formyl group. The acetyl group should rotate 180° so as to locate the methyl group inside the molecule when the aldol reaction occurs. The transannular distance between the benzene carbons bearing acetyl and formyl groups (3.27 Å) is longer than the average transannular distance between the two benzene rings (3.10 Å).

In the original route, however, the starting **6** is tedious to get 10-g quantities of the sample because the TosMIC coupling[20] between 1,3,5-tris(bromomethyl)benzene and TosMIC[21] resulted in low yield (15−20%).[9a] Therefore, we examined an improved route starting from [3₂](1,3)CP **7**,[22] which is much more readily available than **6**. We previously reported the high yield synthesis of [3₄](1,2,4,5)CP **5** by the TosMIC coupling between tetrakis-(bromomethyl)[3₂](1,3)CP **12b**[22] and TosMIC in the presence of NaH in DMF at room temperature (74%), followed by treatment of the resultant cyclic TosMIC adduct **13** with Li in liquid NH₃ in the presence of EtOH (85%) (Scheme 3).[22] The

important synthetic intermediate, the bromide **12b**,[23,24] was prepared by the chloromethylation of **7** (92%) and subsequent halogen exchange of the resultant tetrakis(chloromethyl)[3₂]-(1,3)CP **12a** with NaBr−EtBr in DMF (86%).[22]

Acetylation of **5** with Ac₂O in refluxing CS₂ in the presence of AlCl₃ provided the monoacetyl compound **14** (45%, 52% based on recovered **5**) along with the diacetyl compound **15** (15%, Scheme 3). The structures of **14** and **15** were confirmed by the X-ray structural analyses. Similar to the structure of **9**, the acetyl group is perpendicular to the plane of the attached benzene ring in both cases, and all of the carbonyl oxygen atoms are directed toward the inside of the molecules. It is worth noting that the two acetyl groups of **15** are not located at the pseudogeminal position but in the pseudopara position. Exclusive formation of the pseudopara isomer is ascribed to the steric reason when two acetyl groups are introduced in the pseudogeminal position. The two benzene rings of **14** do not lie directly above one another, being slightly displaced from such an arrangement, and the magnitude (1.0 Å) is more significant in the diacetyl **15** than in **14**. This is because of the severe repulsive steric interaction between carbonyl groups and neighboring trimethylene bridges.

The formylation of **14** with CH₃OCHCl₂ in CH₂Cl₂ in the presence of AlCl₃ provided the *pseudogem*-acetylformyl[3₄]-(1,2,4,5)PC **16** (90%) (Scheme 3). Intramolecular aldol condensation of **16** under alkaline conditions (3 N NaOH) in a mixture of MeOH and THF at reflux afforded the enone **17** (94%), which was readily hydrogenated in the presence of 10%

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Scheme 4. Synthesis and Attempted Double Aldol Condensation of Diacetyl−Diformyl Compound **20**[a]
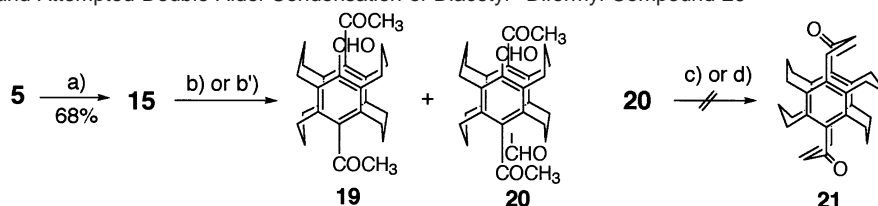
[a] (a) (CH₃CO)₂O, AlCl₃, CH₂Cl₂; (b) CH₃OCHCl₂, AlCl₃, room temperature; (b′) CH₃OCHCl₂, AlCl₃, reflux; (c) 3 N aqueous NaOH, THF, CH₃OH; (d) NaH, DMF.

Pd/C to give the ketone **18** (80%). The ¹H NMR spectrum of the enone **17** shows the aromatic and olefinic proton signals at 6.98 (s) and 7.12 ppm (s) as well as 6.78 (d, J = 12.1 Hz) and 7.77 ppm (d, J = 12.1 Hz), respectively. Reduction of the carbonyl group of **18** by the mixture of AlCl₃ and LiAlH₄ afforded [3₅]CP **3** (75%).[8b,9b] The synthesis of [3₆]CP **2** from **3** was attained according to similar procedures reported by us (Scheme 2).[8b]

The crystal structural properties of *pseudogem*-acetylformyl-[3₄](1,2,4,5)CP **16** are almost the same as those of the *pseudogem*-acetylformyl[3₄](1,2,3,5)CP **9**. In sharp contrast to the molecular structures of the monoacetyl- and diacetyl compounds **14** and **15**, the two benzene rings are completely stacked in **16**. The enone bridge of **17** takes a planar structure, and the two neighboring trimethylene bridges are away from the enone bridge. The crystal structure of [3₅](1,2,3,4,5)-cyclophane-1-one **18** resembles that of [3₅]CP **3**. The transannular distance (2.93 Å) between the benzene carbons bridged with the −COCH₂CH₂− unit is shorter than other distances (3.05 and 3.22 Å).

Furthermore, we studied an alternative approach for the synthesis of **2** via *pseudopara*-diacetyl-[3₄](1,2,4,5)CP **15** (Scheme 4). If two formyl groups are introduced into **15** in one step, double aldol condensations should occur. The formylation of **15** with CH₃OCHCl₂ as both a reagent and a solvent in the presence of AlCl₃ at room temperature exclusively provided the mono-formyl **19** (95%), whereas the desired diformyl **20** was obtained (32%) when the reaction was performed at reflux. The ¹H NMR spectra of **19** and **20** show the formyl proton signals at 10.5 and 10.6 ppm, respectively. The intramolecular aldol condensation of the *pseudogem*-acetylformyl **20** under alkaline conditions (3 N NaOH) did not give the desired enone **21**, but the recovery of the starting material. The use of a stronger base such as NaH in DMF resulted in polymerization. When the aldol reaction occurs, the carbonyl oxygen atom of the acetyl group located inside the molecule must rotate, and the methyl group should be directed toward the formyl carbonyl. However, this rotation must be inhibited by the strong steric constraints in **20**. Therefore, this approach is not promising at this stage.

Thus, we developed an alternative route to **3** starting from [3₂](1,3)CP **7** via [3₄](1,2,4,5)CP **5**. In this route, **5** was obtained from **7** in nine steps in 14% overall yield, whereas the original route (Scheme 2) afforded **3** from [3₃](1,3,5)CP **6** in 10 steps in 20% overall yield. The fact that the starting **7** can be readily prepared in 10-g quantities as compared to **6** makes the route more practical. The construction of two bridges in one step (**20** → **21**) was unsuccessful. Crystallographic data and refinement details are described in the Supporting Information.

2.2. Structural Properties of Multibridged [3ₙ]Cyclophane in the Solid State. [3ₙ]CPs are mobile in solution,[8b,c] and their
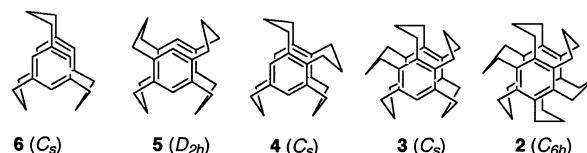
Figure 2. The most stable conformers of multibridged [3ₙ]CPs (n = 3−6) in solution.
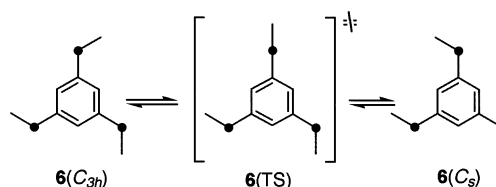
Figure 3. Flipping process of a trimethylene bridge of [3₃](1,3,5)CP **6**.

conformational isomerism is ascribed to the flipping process of the trimethylene bridges. In our continuing efforts, we have studied their conformational behavior in solution by the VT NMR method and theoretical calculations.[8b,c,9,10] The most stable conformers are summarized in Figure 2. However, their structural properties in the solid state have not yet been determined except for that of [3₄](1,2,4,5)CP **5**.[22] We describe here the fundamental structural parameters of [3ₙ]CPs in the solid state.

[3₃](1,3,5)Cyclophane. Two conformers with C_{3h} and C_s symmetries are conceivable in **6** (Figure 3),[9a] and the C_s isomer is more stable than the C_{3h} isomer by 0.4 kcal/mol based on the VT ¹H NMR study in CD₂Cl₂. The energy barrier ($\Delta G^{\ddagger}$) for the bridge flipping process involving **6** (TS) as a transition state is 12.4 kcal/mol (T_c = −70 °C),[9a] and the value is slightly higher than those of [3₂](1,3)-[25,26] and [3₂](1,4)CPs.[27,28]

The structure of the preferred isomer **6** (C_s) in solution is found in the crystalline state at −180 °C. The disorder of the C7−C8 or C9−C10 bridges may result from the presence of the C_s and C_s' conformers in a 1:1 ratio in the crystal packing (Figure 4). The neighboring two cyclophane molecules are in an orthogonal position, and this arrangement is generally

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Table 1. Structural Parameters of [3$_n$]Cyclophanes (*n* = 3−6)

|	[3$_3$]CP **6** C_s	[34](1, 2, 3, 5)CP **4** C_s	[3$_3$]CP **3** C_s	[36]CP **2**-TCNO-F$_4$ (1:1)^a C_{6h}
transannular distances (Å) between benzene rings	C1−C16 3.127(6^b) C2−C11 3.089(6) C3−C12 3.125(6^b) C4−C13 3.093(6^b) C5−C14 3.139(6^b) C6−C15 3.082(6^b)	C1−C15 3.198(2) C2−C10 3.125(2) C3−C11 3.190(2) C4−C12 3.076(2) C5−C13 3.978(2) C6−C14 3.049(2)	C1−C15 3.245(5) C2−C10 3.069(4) C3−C11 3.953(4) C4−C12 3.933(4) C5−C13 3.937(4) C6−C14 3.053(4)	C1−C4* 2.934(2) C2−C5* 2.931(2) C3−C6* 2.929(2)
bond lengths (Å)				
C$_{aromatic}$−C$_{aromatic}$	1.383(6)−1.407(6)	1.393(2)−1.415(3)	1.381(5)−1.420(4)	1.406(2)−1.415(2)
C$_{aromatic}$−C$_{aliphatic}$	1.515(6)−1.549(8)	1.515(2)−1.535(2)	1.518(4)−1.541(4)	1.520(2)−1.523(2)
C$_{aliphatic}$−C$_{aliphatic}$	1.524(8)−1.536(9)	1.541(2)−1.554(2)	1.537(5)−1.553(5)	1.543(3)−1.552(3)
dihedral angles (deg)	122, 126	123, 124, 129, 136	127, 124, 143, 142, 139	140, 142, 142

^{a} Reference 29. ^{b} Estimated standard deviations in the least significant figure are given in parentheses.
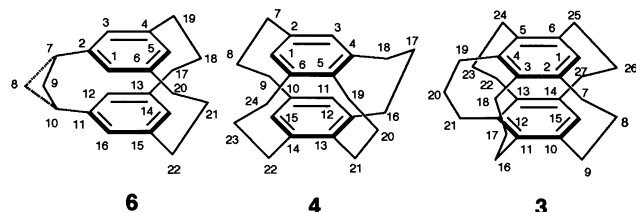
Figure 4. Atom numbering structures of [3$_3$](1,3,5)-, [3$_4$](1,2,3,5)-, and [3$_5$](1,2,3,4,5)CPs **6**, **4**, **3** for X-ray structural data.

observed in the crystal structures of all [3$_n$]CPs. The transannular distances between the two benzene rings are 3.082(7)−3.139-(7) Å. The bond lengths of the benzene rings (1.383(6)−1.407-(6) Å) are comparable to those estimated by the ab initio MO calculations (1.401−1.402 Å, RHF/6-31G).[9c] Similarly, the observed C$_{aromatic}$−C$_{aliphatic}$ [1.515(6)−1.549(8) Å] and C$_{aliphatic}$−C$_{aliphatic}$ bond lengths [1.524(8)−1.536(9) Å] agree well with those predicted by the MO calculations for the former [1.522 (B3LYP) and 1.518 (RHF/6-31G)] and for the latter [1.550 (RHF/6-31G)].[9c] The distances of C7−C8, C7−C9, C8−C10, C9−C10, etc., are unusual because of the large thermal factors due to disorder of the bridge. The dihedral angles of the bridges (C4−C19−C17−C13 and C19−C18−C17 or C6−C20−C22−C15 and C20−C21−C22) are 126 and 122°, respectively, and these values are in good agreement with those expected by the MO calculations (123°, RHF/6-31G) for the C_s structure.[9c]

[3$_4$](1,2,3,5)Cyclophane. [3$_4$](1,2,3,5)CP **4** is observed as the C_s structure in the crystals at −150 °C, which is the most stable conformer estimated by the MO calculations. The neighboring two cyclophane molecules also face in an orthogonal position, similar to the crystal packing diagram of **6**. The transannular distances between the two benzene rings of the cyclophane are 2.978(2)−3.198(2) Å; the C5−C13 distance (2.978 Å) is the shortest among them, whereas the unbridged C1−C15 distance (3.198 Å) is much longer than the corresponding distance of **6** (Figure 4). These data reflect the specific deformation of the benzene rings of **4**. The bond lengths of the benzene rings and the C$_{aromatic}$−C$_{aliphatic}$ and C$_{aliphatic}$−C$_{aliphatic}$ bond lengths are listed in Table 1. The dihedral angle between the C2−C7−C9−C10 and C7−C8−C9 planes is 123°, and other dihedral angles (C4−C18−C16−C12 and C18−C17−C16, C5−C19−C21−C13 and C19−C20−C21, or C6−C24−C22−C14 and C24−C23−C22) are 129, 136, and 124°, respectively. The dihedral angle (136°) of the interposed bridge is greater than the other dihedral angles.

[3$_5$](1,2,3,4,5)Cyclophane. Two conformers of **3a** and **3b** were observed in a ratio of 1.0:1.2 at −70 °C in the ^{1}H NMR
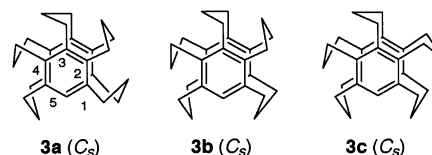
Figure 5. Stable conformers of [3$_5$](1,2,3,4,5)CP **3**.

spectrum in CD$_2$Cl$_2$. The energy barrier ($\Delta G^\ddagger$) for the flipping process was 9.6 kcal/mol (T_c = −70 °C).[9b] MM3 calculations supported the experimental results: **3b** is the most stable among the possible three conformers, and **3a** and **3c** are less stable than **3b** by 0.69 and 1.31 kcal/mol, respectively (Figure 5). The $\Delta G^\ddagger$ corresponds to the flipping of the bridges at C-1 and C-5 because the MM3 calculations[9b] indicated that the energy barrier for the flipping of the trimethylene bridges at C-2 and C-4 (5.4−6.7 kcal/mol) as well as C-3 (5.5 kcal/mol) is considerably reduced as compared to those at C-1 and C-5 (9.5−10.4 kcal/mol).

[3$_5$](1,2,3,4,5)CP **3** (−160 °C) is observed as the most stable C_s structure **3b** in the crystals. The neighboring two cyclophane molecules face an orthogonal position as usual. The transannular distances between the two benzene rings of **3** [C5−C13 (2.937 Å), C4−C12 (2.933 Å), and C3−C11 (2.953 Å)] are shorter than the corresponding distances of **6** (Figure 4). The C4−C12 distance is the shortest, while that of the unbridged C1−C15 (3.245 Å) is the longest among them. The bond lengths of the benzene rings and the C$_{aromatic}$−C$_{aliphatic}$ and C$_{aliphatic}$−C$_{aliphatic}$ bond lengths are normal (Table 1). The dihedral angles of the outer bridges are normal (C2−C7−C9−C10 and C7−C8−C9 as well as C6−C25−C27−C14 and C25−C26−C27 planes are 127 and 124°, respectively), while the dihedral angles of the inner bridges are greater than those of the outer bridges (C3−C18−C16−C11 and C16−C17−C18, C4−C19−C21−C12 and C19−C20−C21, C5−C24−C22−C13 and C22−C23−C24 planes are 143, 142, 139°, respectively), probably because of the steric repulsion of the neighboring bridges.

[3$_6$](1,2,3,4,5,6)CP. In the ^{1}H NMR spectrum of **2** in toluene-d_6, rapid flipping of the six trimethylene bridges is observed. The spectrum exhibits strong temperature-dependent phenomena, and the molecule is frozen as a single conformer with a high symmetry at −70 °C. The energy barrier ($\Delta G^\ddagger$) for this process is 10.9 kcal/mol (T_c = −40 °C) based on the VT NMR spectrum.[8b] The ab initio MO calculations supported the stepwise mechanism where the bridges change their conformation step by step via the TS structure of **2d**, and **2c** is not a TS structure but a local minimum on the potential surface at the

Scheme 5. Expected Trimethylene Bridge Flipping Process: Stepwise Mechanism
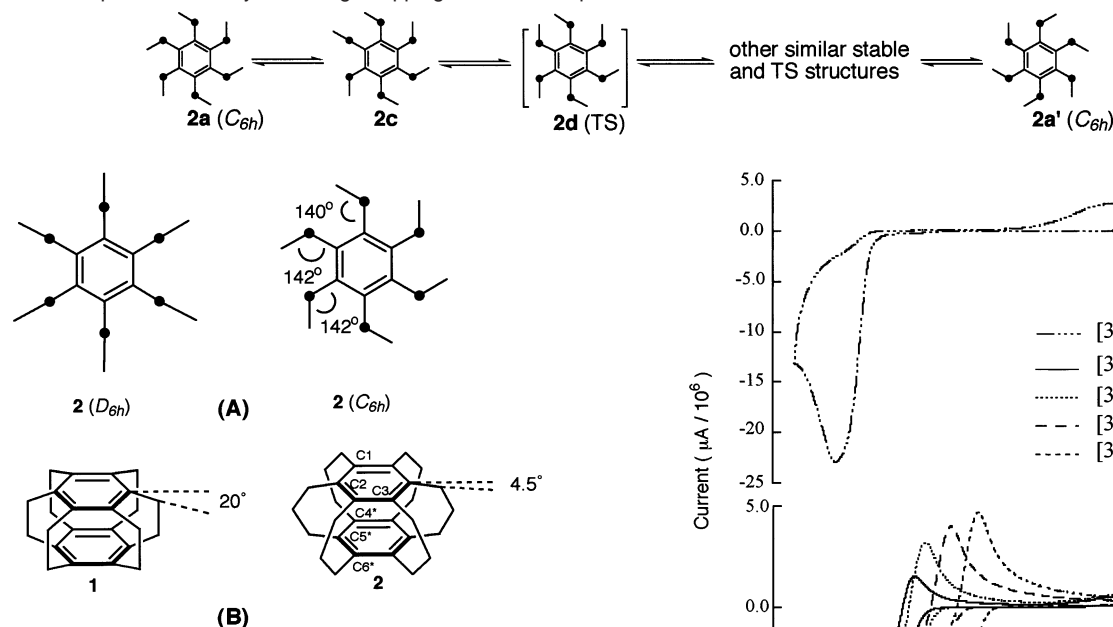
Figure 6. The crystal structures of the cyclophane moieties of the CT complexes of the cyclophane **2**:TCNQ:benzene (1:1:1) (D_{6h}) and **2**:TCNQ-F_4 (1:1) (C_{6h}) at −180 °C (A), and the bending of the benzylic methylene groups out of the plane of the attached benzene ring (B).

RHF/6-31G level of theory (Scheme 5).[9c,10] The flipping of the first bridge induces the flipping of the second bridge adjacent to the first bridge due to the steric repulsion, and the second induces the third, and so on. Thus, the interconversion between **2a** and **2a′** occurs in a stepwise manner.

We briefly describe here the X-ray structural study of **2** because we already reported their result as a communication.[29] The first crystal structure of **2** was examined by using **1**-TCNQ-benzene (1:1:1) complex at −190 °C. In the crystal, a cyclophane (donor) and a TCNQ (acceptor) are stacked, and the benzene ring of the cyclophane and the six-membered ring of the TCNQ partially overlap each other. In the crystal packing diagram, an alternate D−A stacking is observed, and these D−A columns are bound to each other by benzene molecules via CH−π interactions (2.64 Å) between an olefinic proton of the TCNQ and a benzene ring. However, the cyclophane moiety is observed as a D_{6h} conformation due to severe disorder of the molecule with C_{6h} symmetry (Figure 6). The free **2** (−180 °C) also takes the same D_{6h} structure in the crystals due to a disorder problem. No structural differences are observed in the cyclophane moieties of **2** and its TCNQ complex. In contrast to this, the cyclophane moiety of the **2**-TCNQ-F_4 (1:1) complex shows the C_{6h} structure in the crystals. The bending of the benzylic methylene groups out of the plane of the attached benzene ring of the free **2** is 4.5°, and the value is much smaller than that of [2_6]CP **1** (20°).[30] This reflects the much lower molecular strain of **2** than that of **1**. The dihedral angles of the bridges are 140°, 142°, and 142°, and these values are in good agreement with those expected by the MO calculations (142° by RHF/6-31G) for the C_{6h} structure.[9c,10]

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(30) Hanson, W.; Cameron, T. S. *J. Chem. Res., Synop.* **1980**, 336−337.
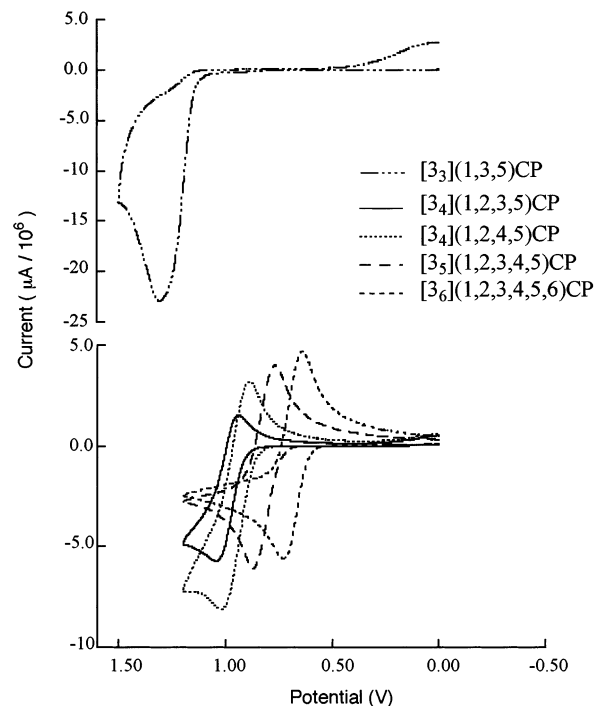
Figure 7. Cyclic voltammograms of [3_n]CPs ($n = 3−6$) in $Cl_2CHCHCl_2$/0.1 M Bu_4NPF_6 observed at a potential scan rate of 20 mV s^{-1}.

The crystal structural analyses of [3_n]CPs have been successfully accomplished, and the observed structures are, in principle, in good agreement with the most stable conformers found in solution and predicted by the theoretical calculations. Although the ^{1}H NMR spectrum at low temperatures and theoretical calculations predicted that the most stable conformation of [3_6]CP **2** was a C_{6h} structure, the highly strained D_{6h} structure was observed both in the crystals of **2** itself and in the **2**:TCNQ:benzene (1:1:1) complex. However, the C_{6h} structure was observed in the crystal structure of the **2**-TCNQ-F_4 (1:1) complex, which suggests that the most stable conformer is C_{6h} in the crystals. The D_{6h} structure in the crystals of **2** and its TCNQ complex may result from the presence of the **2**(C_{6h}) and **2′**(C_{6h}) conformers in a 1:1 ratio in the crystal packing.

2.3. Electric and Structural Properties of the Charge-Transfer Complexes of the [3ₙ]Cyclophanes with Acceptors. As described above, the electron-donating ability of [3_n]CPs is increased with an increase in the number of the bridges, and **2** shows the strongest donating ability. This tendency is also clearly observed in the cyclic voltammograms (CVs) of [3_n]CPs in $Cl_2CHCHCl_2$ (Figure 7). Quite interestingly, [3_4](1,2,3,5)-CP **4**, [3_4](1,2,4,5)CP **5**, [3_5]CP **3**, and [3_6]CP **2** show reversible redox processes. The first half-wave oxidation potential [$E_{1/2}$ (I)] decreased as the number of the bridge increased (Table 2): +0.69 (**4**), +0.66 (**5**), +0.51 (**3**), and +0.39 (**2**) V (vs F_c/F_c^+). The CV of **6**, however, does not show reversibility, and the anodic peak E_{pa} appears at +1.01 V (vs F_c/F_c^+, 1.31 V vs Ag/AgCl). This suggests a much lower electron-donating ability of **6** than the higher homologues. The $E_{1/2}$ (I) data correspond

Table 2. Oxidation Potentials of [3$_n$]Cyclophanes (n = 3−6)^a

compound	$E_{1/2}$ (I) (V vs F_c/F_c^+)	E_{pa} (I) (V vs Ag/AgCl)
[3$_3$](1,3,5)CP		1.31
[3$_4$](1,2,3,5)CP	+0.69	1.04
[3$_4$](1,2,4,5)CP	+0.66	1.02
[3$_5$](1,2,3,4,5)CP	+0.51	0.87
[3$_6$](1,2,3,4,5,6)CP	+0.39	0.73

^{a} In 1,1,2,2-tetrachloroethane containing 0.1 M Bu$_4$NPF$_6$; scan rate 20 mV/s.

to the increase in the first HOMO level as the number of the bridges increases, and, hence, the HOMO−LUMO gaps decrease. Therefore, [3$_n$]CPs may be promising candidates for new donor molecules for the development of new electron-conducting materials.

By taking advantage of the strong electron-donating ability of [3$_n$]CPs, we prepared their CT complexes with relatively strong electron acceptors, such as TCNQ and TCNQ-F$_4$, and examined their electric and structural properties. When [3$_n$]CP is mixed with TCNQ in CHCl$_3$, the color of the solution changes to black or dark blue, the CT bands of the TCNQ complexes appear in a longer wavelength region than the corresponding complexes of TCNE, and the CT bands show a bathochromic shift (62−70 nm) as the number of the bridge increases [λ_{max} (CHCl$_3$) [3$_3$](1,3,5)CP **6** 658; [3$_4$](1,2,3,5)CP **4** 724; [3$_5$]CP **3** 854; [3$_6$]CP **2**; 916 nm].

The single-crystal conductivity data of the CT complexes of [3$_n$]CPs with TCNQ and TCNQ-F$_4$ are summarized in Table 3.[31] The data of the **5** and **4** complexes are missing because the cyclophane reacted with acceptors in the former or suitable crystals were not obtained in the latter. The conductivities of the TCNQ complexes are in the range of 4 × 10^{-9}−5 × 10^{-8} S cm^{-1}, and they are insulators. Relatively high conductivities are observed in the TCNQ-F$_4$ complexes. Although the direct comparison of the data is difficult because of different stoichiometries of the components, the TCNQ-F$_4$ complexes are much more conductive than the corresponding TCNQ complexes mainly due to larger charge separation as is shown by the ν_{CN} (cm^{-1}) data; the **2**-TCNQ-F$_4$ (1:1) complex shows a conductivity of the order of 10^{-6} S cm^{-1}, while that of the corresponding TCNQ complex is on the 10^{-9} S cm^{-1} order. The conductivity does not depend on the electron-donating ability of the cyclophane; the **6**-TCNQ-F$_4$ (1:1) complex is more conductive by 100 times than the corresponding **2** complex. To clarify this anomalous phenomenon and to examine the dependence of the conductivity on the structural properties, we have studied the X-ray crystal structures for a series of CT complexes.

In the crystal structure of the **6**-TCNE (1:1) complex at −180 °C, each TCNE lies on or near a center of symmetry in a sandwich arrangement between two cyclophane molecules, and this leads to a 1:1 complex with alternate D−A stacking. The TCNE molecules are almost parallel to the associated phenyl rings. The plane-to-plane average distance is 3.22 Å, similar to those found in [2$_2$](1,4)CP-TCNE (3.3 Å)[19b] and other cyclophane-TCNE complexes.[18,19] The average transannular distance between the two benzene rings is 3.11 Å.

The **6**-TCNQ complexes were obtained as two crystalline modifications. The **6**-TCNQ (2:1) complex was obtained as prisms from CH$_2$Cl$_2$−CH$_3$CN, whereas the **6**-TCNQ (4:1)

complex was obtained as plates from CH$_2$Cl$_2$−MeOH. In the crystal structure of the **6**-TCNQ (2:1) complex at −180 °C, a cyclophane and a TCNQ are stacked with the D−A distance being 3.26 Å, and the benzene ring of the cyclophane and the TCNQ partially overlap each other, similar to the crystal structure of the **2**-TCNQ-F$_4$ (1:1) complex.[29] The average transannular distance between the two benzene rings is 3.12 Å. The cyclophane is observed as C_s and C_{3h} conformations due to the disorder of the molecule. Each cyclophane interacts with TCNQ on only one face of the molecule. As a result, two cyclophane molecules coordinate with a TCNQ, and this leads to a 2:1 complex. In the crystal structure of the **6**-TCNQ (4:1) complex at −180 °C, a similar D−A overlap is observed for a cyclophane and a TCNQ with the D−A distance of 3.39 Å. The other cyclophane interacts with an olefinic proton of the TCNQ through the CH−π interaction (2.90 Å), and the 4:1 unit is formed. Thus, the donor and acceptor are bound with CT and CH−π interactions.

In the crystal structure of the [3$_5$]CP **3**-TCNQ (1:1) complex at −180 °C, a D−A overlap (3.25 Å) similar to those of the **6**-TCNQ (2:1) and **2**-TCNQ-F$_4$ (1:1) complexes[29] is observed. In the crystal packing diagram, an alternate D−A stacking is observed. The cyclophane structure takes the C_s conformation, and disorder of a bridge is observed, which may be ascribed to the similar stabilities of the **3a** and **3b** conformers as described above (Figure 5). The crystal structural properties of the **2**-TCNQ-benzene (1:1:1) complex at −190 °C were already described in a communication[29] and, therefore, will not be described here.

In general, it is believed that electrons move through the column of acceptors. Therefore, the distance of the partially overlapped acceptors in the column may be an important factor for high conductivity. In solution, a strong association of [3$_n$]-CPs with TCNQ was observed, but only a weak electronic charge separation due to the CT interaction was detected in the solid state. The charge separation of the crystals of the **2**-TCNQ-benzene (1:1:1) is ca. 0.1−0.2 according to the method reported by Bloch et al.[32]

The cyclophane moiety of the **6**-TCNQ-F$_4$ (1:1) complex shows a C_s structure in the crystals. The D−A overlapping mode is similar to that of **6**-TCNQ, and the transannular D−A distance is 3.32 Å. The partially overlapped acceptors are regularly stacked with a distance of 2.93 Å and form an infinite column (Figure 8A). The acceptors in the unit cell are arranged parallel in a plane with an A−A distance of 3.14 Å (Figure 8B).

The cyclophane moiety of the **4**-TCNQ-F$_4$ (1:1) complex shows a C_s structure in the crystals. The overlapping mode of the donor and acceptor is similar to that of the **6**-TCNQ-F$_4$ (1:1) complex. An alternating D−A stacking similar to that of **2**-TCNQ-F$_4$ (1:1) is observed in the crystal packing diagram. The distance between acceptors in the unit cell is 3.25 Å. The cyclophane moiety of the **3**-TCNQ-F$_4$ (1:1) complex shows the two C_s structures in the crystals. An alternating D−A stacking similar to that of **3**-TCNQ is observed in the crystal packing diagram. The distance between the acceptors in the unit cell is 3.42 Å.

The cyclophane moiety of the **2**-TCNQ-F$_4$ (1:1) complex shows the C_{6h} structure in the crystals (Figure 6).[29] The

(31) Electrical conductivities were measured with a two probe method.

(32) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442−2443.

Table 3. Conductivities of the [3n]Cyclophane-TCNQ or TCNQ-F4 Complexes in the Single Crystals, and the Transannular Donor−Acceptor Distance, Average Transannular Distance between Two Benzene Rings, and Acceptor−Acceptor Distance of the Charge-Transfer Complexes in the Solid State

charge-transfer complexes	σ (S cm^{-1})	ν_{CN} (cm^{-1}, KBr)	D−A distance (Å)	distance between two benzene rings (Å)	acceptor−acceptor distance (Å)
[3$_3$]CP **6**−TCNE (1:1)			3.22	3.11 (3.08−3.14)^a	4.11
[3$_3$]CP **6**−TCNQ (2:1)			3.26	3.12	
[3$_3$]CP **6**−TCNQ (4:1)	5.0×10^{-8}	2218	3.48	3.11, 3.12	
[3$_3$]CP **6**−TCNQ-F$_4$ (1:1)	2.1×10^{-4}	2219	3.32	3.11	2.93, 3.14
[3$_4$]CP **4**−TCNQ-F$_4$ (1:1)	2.3×10^{-9}	2217	3.20	3.05 (2.98−3.20)	3.25
[3$_5$]CP **3**−TCNQ (1:1)		2214	3.25	2.94 (2.93−3.25)	
[3$_5$]CP **3**−TCNQ-F$_4$ (1:1)	<8.0×10^{-9}	2219	3.19	3.02	3.42
[3$_6$]CP **2**−TCNQ−C$_6$H$_6$ (1:1:1)^a	4.4×10^{-9}	2216	3.34	2.94 (2.93)	
[3$_6$]CP **2**−TCNQ-F$_4$ (1:1)^a	6.1×10^{-6}	2217	3.22	2.94	3.22

^{a} TCNQ 2220 cm^{-1}, TCNQ-F$_4$ 2237 cm^{-1}; transannular distances between two benzene rings of the cyclophane (Å).
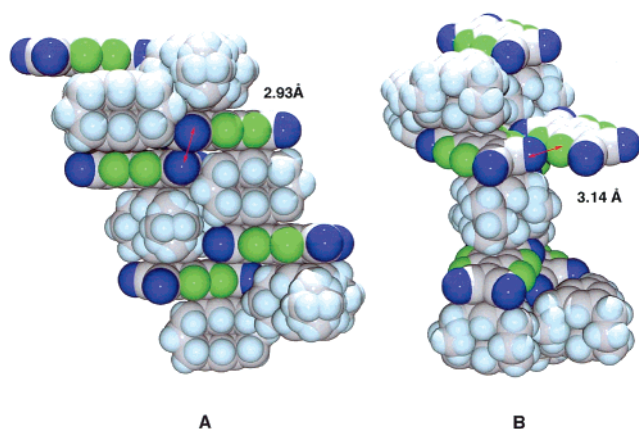
Figure 8. ORTEP drawings (CPK model) of the crystal packing diagram of [3$_3$](1,3,5)CP **6**-TCNQ-F$_4$ (1:1) complex at −180 °C (side views).
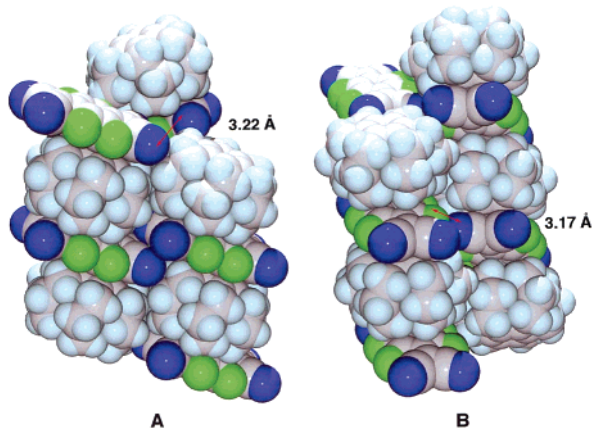
Figure 9. ORTEP drawings (CPK model) of the crystal packing diagram of [3$_6$]CP **2**-TCNQ-F$_4$ (1:1) complex at −180 °C (side views).

transannular D−A distance is 3.22 Å, and the average transannular distance between the two benzene rings is 2.94 Å. Partially overlapped acceptors are stacked with a distance of 3.22 Å (Figure 9A), and the acceptors in the unit cell are arranged parallel in a plane with the A−A distance being 3.17 Å (Figure 9B).

We found that the **6**-TCNQ-F$_4$ (1:1) complex is much more conductive than the corresponding **2**-TCNQ-F$_4$ complex, irrespective of the much higher electron-donating ability of **2**, and this may be ascribed to the formation of an infinite column of partially overlapped acceptors with a much shorter A−A distance than that of the **2**-TCNQ-F$_4$ complex and the close

contact of the acceptors arranged parallel in a plane of the unit cell (Figure 8).

3. Conclusions

The fact that the starting [3$_2$](1,3)CP **7** is much more readily prepared in 10-g quantities than [3$_3$](1,3,5)CP **6** makes the improved route more practical than the original one. The crystal structural analyses of [3$_n$]CPs were successfully accomplished, and the observed structures were in good agreement with the most stable conformers in solution and predicted by the theoretical calculations. The highly strained structure with a D_{6h} symmetry was observed in the crystal structure of **2** and the **2**:TCNQ:benzene (1:1:1) complex, and this is ascribed to the presence of the **2**(C_{6h}) and **2'**(C_{6h}) conformers in a 1:1 ratio in the crystal packing. The C_{6h} structure was observed in the crystal structure of the **2**-TCNQ-F$_4$ (1:1) complex. This study revealed the fundamental structural parameters of [3$_n$]CPs in the solid state. The first half-wave oxidation potential [$E_{1/2}$ (I)] of **2** [+0.39 V vs F_c/F_c^+, Cl$_2$CHCHCl$_2$] supports its strong donating ability. This is attributed to the molecular structure where effective hyperconjugation between the benzyl hydrogens and benzene ring is possible.

Among the [3$_n$]CP-TCNQ complexes, the [3$_3$](1,3,5)CP **6**-TCNQ-F$_4$ (1:1) complex showed the highest conductivity, and this may be ascribed to the formation of an infinite column of partially overlapped acceptors with a short A−A distance and the close contact of the acceptors arranged parallel in a plane of the unit cell. Although the conductivities of our CT complexes are much lower than those of the TTF related[33] or non-TTF related complexes,[34,35] our study successfully provides the basic knowledge for the understanding of the CT interactions in the solid state.

For the development of electron conductors and superconductors, structural studies in the solid state are indispensable. For example, the first organic metal complex, TTF-TCNQ, was shown to have segregated columns of donor and acceptor molecules.[36] We expect that the overlapping modes and crystal packing of a donor and an acceptor might be controlled by the

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modification of the donating ability of a donor. Control of the D−A overlapping modes, transannular D−A distances, and crystal packings[37] may be possible by the modification of the benzene rings of [3_n]CPs. Our synthetic and solid-state structural studies of the heteroanalogues of [3_n]CPs are now in progress, and the results will be reported elsewhere.

4. Experimental Section

4.1. General Procedures. Melting points were measured on a Yanako MP-S3 micro melting point apparatus. ^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-GX 270 and AL-300 spectrometers. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (TMS) in CDCl[3] unless otherwise noted. Mass spectra (EIMS ionization voltage 70 eV) and fast atom bombardment mass spectra (FAB-MAS, *m*-nitrobenzyl alcohol) were obtained with a JEOL JMS-SX/SX 102A mass spectrometer. Electronic spectra were recorded on a Hitachi U-3500 spectrometer. Infared data were obtained on a Hitachi Nicolet I-5040 FT-IR spectrometer. Elemental analyses were performed by the Service Centre of the Elemental Analysis of Organic Compound affiliated with the Faculty of Science, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on Silica gel 60 F[254] Merck. Column chromatography was performed on Merck Silica gel 60 (40−63 μm). All solvents and reagents were of reagent quality, purchased commercially, and used without further purification, except as noted below. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. DMF was dried with molecular sieves 4 A. 1,1,2,2-Tetrachloroethane was dried with CaCl[2] and distilled just before use.

[3_2](1,3)CP **7**[22] and [3_3](1,3,5)CP **6**[9a] were prepared according to the reported procedures. [3_4](1,2,4,5)CP **5** was synthesized from **7** according to the reported procedures.[22] *p*-Toluenesulfonylmethyl isocyanide (TosMIC)[21] was prepared by the dehydration of *p*-toluenesulfonylmethyl formamide with POCl[3] in dioxane−Et[2]O at −10 °C.

Cyclic voltammograms were recorded by a BAS-100 B/W electron chemical analyzer. A Pt wire counter electrode and a Ag/0.01 M AgNO[3] reference electrode were used. The measurements were carried out in 0.1 M 1,1,2,2-tetrachloroethane solution of a substrate using Bu[4]NPF[6] as supporting electrolyte, and the oxidation potential values were calibrated with ferrocene.

X-ray Crystallographic Study. The X-ray structural analyses were obtained with Rigaku RAXIS-IV [**3**, **4**, **9**, **15**, [3_5]CP-TCNQ (1:1)] and RAXIS-RAPID [**6**, **14**, **16**, **17**, **18**, [3_3](1,3,5)CP-TCNE (1:1), [3_3]-(1,3,5)CP-TCNQ (2:1), [3_3](1,3,5)CP-TCNQ (4:1), [3_3](1,3,5)CP-TCNQ-F[4] (1:1), [3_4](1,2,3,5)CP-TCNQ-F[4] (1:1), [3_5]CP-TCNQ-F[4] (1:1)] imaging plate diffractometers with graphite monochromated Mo Kα radiation. The crystal structure was solved by the direct method [SIR88[38] (**16**, [3_3](1,3,5)CP-TCNQ (4:1), [3_4](1,2,3,5)CP-TCNQ-F[4] (1:1)), SIR92[39] (**3**, **4**, **9**, **15**, **17**, **18**, [3_3](1,3,5)CP-TCNE (1:1), [3_5]CP-TCNQ (1:1), [3_5]CP-TCNQ-F[4] (1:1)), SCHELEX97[40] (**6**, **14**, [3_3](1,3,5)-CP-TCNQ (2:1)), and MITHRIL90[41] ([3_3](1,3,5)CP-TCNQ-F[4] (1:1))] refined by the full-matrix least-squares methods.[40] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined

(36) In the crystal structure of the TTF-TCNQ (1:1) complex, donors and acceptors form segregated columnar stacks, and the TCNQ interplanar distance is 3.17 Å. Phillips, T. E.; Kistenmacher, T. J.; Ferraris, J. P.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1973**, 471−472. (b) Kistenmacher, T. J.; Phillips, T. E.; Cowan, D. O. *Acta Crystallogr.* **1974**, *B30*, 763−768.
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isotopically. All computations were performed using the teXsan package.[42]

4.2. Improved Synthetic Route. 5-Acetyl[3_4](1,2,4,5)cyclophane 14. To a stirred mixture of [3_4](1,2,4,5)cyclophane **5** (400 mg, 1.26 mmol), AlCl[3] (4.00 g, 3.00 mmol), and CS[2] (50 mL) was added a mixture of (CH[3]CO)[2]O (0.15 g, 1.47 mmol) and CS[2] (5 mL) in one portion at room temperature. After the addition, the mixture was refluxed for 12 h with stirring. The reaction mixture was poured into ice water and extracted with CHCl[3]. The combined extracts were successively washed with water and brine, dried with Na[2]SO[4], and filtered. After the solvent was removed, the residue was chromatographed on silica gel with CHCl[3]/hexane (3:1) to give recovered **5** (52 mg, 13%), the desired acetyl compound **14** (205 mg, 45%, 52% based on recovered **5**), and the *pseudopara*-diacetyl compound **15** (76 mg, 15%). **14**: colorless prisms (CHCl[3]), mp 206−208 °C. ^{1}H NMR: δ 2.08−2.72 (m, 16H, $CH_2CH_2CH_2$), 2.17 (s, 3H, COCH[3]), 3.03−3.11 (m, 8H, $CH_2CH_2CH_2$), 6.84 (s, 1H, ArH), 6.93 (s, 1H, ArH), 7.09 (s, 1H, ArH). IR (KBr): ν 1692 (C═O) cm^{−1}. FAB-MS *m/z* M[+] 358. Anal. Calcd for C[26]H[30]O: C, 87.10; H, 8.43. Found: C, 87.23; H, 8.45.

5-Acetyl-14-formyl[3_4](1,2,4,5)cyclophane 16. To a mixture of AlCl[3] (0.93 g, 6.98 mmol) and **14** (1.00 g, 2.79 mmol) in CH[2]Cl[2] (3 mL) was dropwise added a mixture of Cl[2]CHOCH[3] (500 mg, 4.35 mmol) in CH[2]Cl[2] (3 mL) over a period of 5 min in an ice bath with stirring. After the mixture had been stirred in an ice bath for 1.5 h, it was poured into ice water and extracted with CH[2]Cl[2]. The combined extracts were successively washed with water and brine, dried with Na[2]SO[4], and filtered. Removal of the solvent provided **16** (0.97 g, 90%), which was used in the next reaction without further purification. A sample was recrystallized from CH[2]Cl[2] to give pale yellow prisms. **16**: mp > 300 °C. ^{1}H NMR: δ 2.01−2.74 (m, 14H, $CH_2CH_2CH_2$), 2.10 (s, 3H, COCH[3]), 3.06−3.50 (m, 10H, $CH_2CH_2CH_2$), 7.05 (s, 1H, ArH), 7.12 (s, 1H, ArH), 10.51 (s, 1H, CHO). IR (KBr): ν 1667 (C═O), 1696 (C═O) cm^{−1}. FAB-MS *m/z* M[+] 386. Anal. Calcd for C[27]H[30]O[2]: C, 83.90; H, 7.82. Found: C, 83.56; H, 7.78.

[3_5](1,2,3,4,5)Cyclophane-1-ene-3-one 17. To the crude **16** (900 mg, 2.33 mmol) dissolved in a mixture of MeOH (80 mL) and THF (80 mL) was added 3 N aqueous NaOH (80 mL) in one portion, and the mixture was stirred for 24 h at reflux. After the solvent was removed, the aqueous portion was neutralized with diluted HCl, and extracted with CHCl[3]. The combined extracts were washed successively with brine and water, dried with MgSO[4], and filtered. The filtrate was concentrated in vacuo, and the concentrate was chromatographed on silica gel with CHCl[3] to give the enone **17** (812 mg, 94%, 85% from **14**). **17**: colorless prisms (CH[2]Cl[2]), mp 272−273 °C. ^{1}H NMR: δ 1.88−1.93 (m, 2H, CH[2]CH_2CH[2]), 2.24−2.40 (m, 4H, CH[2]CH_2CH[2]), 2.62−2.91 (m, 12H, $CH_2CH_2CH_2$), 3.01−3.17 (m, 6H, $CH_2CH_2CH_2$), 6.98 (s, 1H, ArH), 7.12 (s, 1H, ArH), 6.78 (d, *J* = 12.1 Hz, 1H, CH═CH), 7.77 (d, *J* = 12.1 Hz, 1H, CH═CH). IR (KBr): ν 1646 (C═O) cm^{−1}. FAB-MS *m/z* M[+] 368. Anal. Calcd for C[27]H[28]O: C, 88.00; H, 7.66. Found: C, 88.23; H, 7.64.

[3_5](1,2,3,4,5)Cyclophane-1-one 18. A mixture of **17** (500 mg, 1.35 mmol), 10% Pd/C (300 mg), MeOH (25 mL), and THF (50 mL) was stirred under an atmosphere of H[2] gas for 3 d at room temperature. The Pd/C was removed by filtration, and the filtrate was concentrated in vacuo to give the ketone **18** (403 mg, 80%). **18**: colorless prisms (CH[2]Cl[2]), mp > 300 °C. ^{1}H NMR: δ 2.07−2.39 (m, 8H, −CH[2]CH_2-CH[2]−), 2.67−2.79 (m, 6H, −CH[2]CH[2]CH[2]−), 2.95−3.17 (m, 10H, CH[2]-CH[2]CH[2]), 3.28−3.50 (m, 4H, CH_2CH_2CO), 6.91 (s, 1H, ArH), 6.95 (s, 1H, ArH). IR (KBr): ν 1676 (C═O) cm^{−1}. FAB-MS *m/z* M[+] 370. Anal. Calcd for C[27]H[30]O: C, 87.52; H, 8.16. Found: C, 87.41; H, 8.24.

[3_5](1,2,3,4,5)Cyclophane 3. To a mixture of AlCl[3] (864 mg, 6.48 mmol) and **18** (400 mg, 1.08 mmol) in dry THF (50 mL) was added dropwise a mixture of LiAlH[4] (62 mg, 1.62 mmol) and dry THF (30

(42) Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1999).

mL) over a period of 15 min in an ice-salt bath under argon with stirring. The mixture was allowed to warm to room temperature and then refluxed for 16 h with stirring. The reaction mixture was poured into 6 N aqueous H$_2$SO$_4$, and extracted with CHCl$_3$. The combined extracts were successively washed with water and brine, dried with Na$_2$SO$_4$, and filtered. Removal of the solvent provided white powder, which was purified by silica gel column chromatography with CHCl$_3$/hexane (1:3) to give **3** (289 mg, 0.81 mmol, 75%), whose spectroscopic and physical properties were in complete agreement with those of the reported values.[8b,9b] **3**: colorless prism (hexane), mp 265−267 °C (lit.[8b,9b] 265.0−266.6 °C). ^{1}H NMR: δ 2.10−2.24 (m, 2H, CH$_2$*CH$_2$*-CH$_2$), 2.33−2.57 (m, 8H, CH$_2$*CH$_2$*CH$_2$), 2.65−2.73 (m, 4H, *CH$_2$*-CH$_2$*CH$_2$*), 3.05−3.20 (m, 16H, *CH$_2$*CH$_2$*CH$_2$*), 6.73 (s, 2H, ArH). FAB-MS *m/z* M$^+$ 356.

5,18-Diacetyl[3$_4$](1,2,4,5)cyclophane 15. To a mixture of [3$_4$]-(1,2,4,5)cyclophane **5** (100 mg, 0.51 mmol) and AlCl$_3$ (168 mg, 1.26 mmol) in CS$_2$ (5 mL) and CH$_2$Cl$_2$ (20 mL) was added a solution of (CH$_3$CO)$_2$O (153 mg, 1.5 mmol) in CH$_2$Cl$_2$ (5 mL) in one portion at room temperature with stirring. After the addition, the mixture was refluxed for 2 d with stirring. The reaction mixture was poured into ice water and extracted with CHCl$_3$. The combined extracts were successively washed with water and brine, dried with Na$_2$SO$_4$, and filtered. After the solvent was removed, the residue was chromatographed on silica gel with CHCl$_3$ to give the *pseudopara*-diacetyl compound **15** (86 mg, 68%). **15**: faint orange prisms (CH$_2$Cl$_2$), mp 280−281 °C. ^{1}H NMR: δ 2.32−2.37 (m, 2H, CH$_2$*CH$_2$*CH$_2$), 2.54−2.70 (m, 12H, *CH$_2$CH$_2$CH$_2$*), 3.02−3.15 (m, 10H, *CH$_2$*CH$_2$*CH$_2$*), 2.06 (s, 6H, COCH$_3$), 6.98 (s, 2H, ArH). IR (KBr): ν 1687 (C=O) cm^{-1}. FAB-MS *m/z* M$^+$ + 1, 401. Anal. Calcd for C$_{28}$H$_{32}$O$_2$: C, 83.96; H, 8.05. Found: C, 84.05; H, 8.33.

5,18-Diacetyl-15-formyl[3$_4$](1,2,4,5)cyclophane 19. To a mixture of **15** (50 mg, 0.125 mmol) and CH$_3$OCHCl$_2$ (20 mL) was added AlCl$_3$ (68 mg, 0.50 mmol) portionwise over a period of 2 min in an ice bath with stirring. After the mixture had been stirred at room temperature overnight, it was poured into ice water and extracted with CH$_2$Cl$_2$. The combined organic layer was successively washed with water and brine, dried with Na$_2$SO$_4$, and filtered. After the solvent was removed, the residue was chromatographed on silica gel with AcOEt to give **19** (51 mg, 95%). **19**: faint orange prisms (CH$_2$Cl$_2$), mp > 300 °C. ^{1}H NMR: δ 2.12 (s, 6H, COCH$_3$), 2.03−2.50 (m, 12H, CH$_2$*CH$_2$*CH$_2$), 2.68−2.77 (m, 2H, *CH$_2$CH$_2$CH$_2$*), 3.08−3.38 (m, 10H, *CH$_2$*CH$_2$*CH$_2$*), 7.29 (s, 1H, ArH), 10.53 (s, 1H, CHO). IR (KBr): 1680 (C=O), 1688 (C=O) cm^{-1}. FAB-MS *m/z* M$^+$ 429. Anal. Calcd for C$_{29}$H$_{32}$O$_3$: C, 81.27; H, 7.53. Found: C, 81.35; H, 7.54.

5,18-Diacetyl-8,15-diformyl[3$_4$](1,2,4,5)cyclophane 20. To a mixture of **15** (50 mg, 0.125 mmol) in CH$_3$OCHCl$_2$ (20 mL) was added AlCl$_3$ (68 mg, 0.50 mmol) portionwise over a period of 2 min in an ice bath with stirring. After the mixture had been stirred at reflux overnight, it was poured into ice water and extracted with CH$_2$Cl$_2$. The organic layer was washed with water and brine, dried with Na$_2$SO$_4$,

and filtered. After the solvent was removed, the residue was chromatographed on silica gel with AcOEt to give **20** (18 mg, 0.04 mmol, 32%). **20**: faint orange prisms (CH$_2$Cl$_2$), mp > 300 °C. ^{1}H NMR: δ 2.08 (s, 6H, COCH$_3$), 2.12−2.43 (m, 12H, CH$_2$*CH$_2$*CH$_2$), 3.19−3.50 (m, 12H, *CH$_2$*CH$_2$*CH$_2$*), 10.57 (s, 2H, CHO). IR (KBr): 1673 (C=O), 1688 (C=O) cm^{-1}. FAB-MS M$^+$ + 1, 457. Anal. Calcd for C$_{29}$H$_{32}$O$_3$: C, 78.92; H, 7.66. Found: C, 78.64; H, 7.45.

Preparation of the Charge-Transfer Complexes. General procedure for the preparation of TCNQ and TCNQ-F$_4$ complexes: TCNQ-F$_4$ (10 mg, 0.36 mmol) was dissolved in CHCl$_3$ (10 mL) at room temperature in a 100-mL glass vial, and this solution was added to [3$_3$](1,3,5)CP **6** (10 mg, 0.36 mmol) in CHCl$_3$ (5 mL). The resultant mixture was allowed to stand for 5−6 d until dark blue crystals were formed. The resultant crystals were collected by decantation from the solvent, dark blue prism; IR (KBr): ν 2219 (CN) cm^{-1}.

TCNQ Complexes. The [3$_3$](1,3,5)CP-TCNQ (2:1) complex was obtained by recrystallization from a mixture of CH$_2$Cl$_2$ and CH$_3$CN, dark blue prisms; IR (KBr): ν 2218 (CN) cm^{-1}. Anal. Calcd for C$_{48}$H$_{46}$N$_4$: C, 85.68; H, 6.92; N, 7.40. Found: C, 85.64; H, 6.90; N, 7.38. The [3$_3$](1.3.5)CP-TCNQ (4:1) complex was obtained by the recrystallization from a mixture of CH$_2$Cl$_2$ and MeOH as dark blue plates; IR (KBr): ν 2218 (CN) cm^{-1}. The [3$_5$]CP-TCNQ (1:1) complex was obtained by the recrystallization from CH$_2$Cl$_2$ as dark blue prisms; IR (KBr): ν 2214 (CN) cm^{-1}. The [3$_6$]CP-TCNQ (1:1) complex was obtained by the recrystallization from C$_6$H$_6$ as dark red prisms; IR (KBr): ν 2216 (CN) cm^{-1}. Anal. Calcd for C$_{48}$H$_{46}$N$_4$: C, 84.92; H, 6.83; N, 8.25. Found: C, 84.91; H, 6.83; N, 8.26.

TCNQ-F$_4$ Complexes. The [3$_4$](1,2,3,5)CP-TCNQ-F$_4$ (1:1) complex was obtained by the recrystallization from CHCl$_3$ as dark blue prisms; IR (KBr): ν 2217 (CN) cm^{-1}. The [3$_5$]CP-TCNQ-F$_4$ (1:1) complex was obtained by the recrystallization from CHCl$_3$ as dark red prisms; IR (KBr): ν 2219 (CN) cm^{-1}. The [3$_6$]CP-TCNQ-F$_4$ (1:1) complex was obtained by the recrystallization from CHCl$_3$ as dark red prisms; IR (KBr): ν 2217 (CN) cm^{-1}.

TCNE Complex. The [3$_3$](1,3,5)CP-TCNE (1:1) complex was obtained by the crystallization from CH$_2$Cl$_2$ as dark purple plates; IR (KBr): 2134 (CN) cm^{-1}.

Supporting Information Available: ORTEP drawings and summary of crystallographic data and refinement details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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