Solid-State Structural Study of the Charge-Transfer Complexes of 5,7,9-Trimethyl- and 2,11,20-Trithia[3_3](1,3,5)cyclophanes[‡]

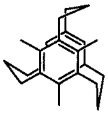
Mikio Yasutake,[a,b,c] Koji Araki,[d] Ming Zhou,[a,b] Rika Nogita,[a,b] and Teruo Shinmyozu*[a]

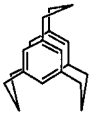
Keywords: Charge transfer / Conformation analysis / Cyclophanes / NMR spectroscopy

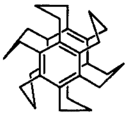
5,7,9-Trimethyl[3_3](1,3,5)cyclophane (**1**), with two binding sites of different donating ability, adopts a C_3 conformation both in the solid state (–170 °C) and in CD_2Cl_2 solution at –90 °C. 5,7,9-Trimethyl[3_3](1,3,5)cyclophane-2,11,20-trione (**9**) has the same C_3 symmetry, while [3_3](1,3,5)cyclophane-2,11,20-trione (**12**) adopts the C_s structure in the solid state (–170 °C). The structures of **1** and **9** are the first examples of C_3 or C_{3h} symmetries in the [3_3](1,3,5)cyclophanes; their preferred conformers are C_s both in solution and in the solid state. The cyclophane **1** shows much stronger donating ability than the parent [3_3](1,3,5)cyclophane (**2**). In the TCNQ-F_4 (1:1) complex of **1**, the donor (D) and the acceptor (A) are stacked alternately, with partial and complete D-A overlaps being observed in the solid state (–170 °C) in the forms of partial D-A overlap of the methyl-substituted benzene face and TCNQ-F_4 and of nearly complete D-A overlap of the methyl-unsubstituted benzene face and TCNQ-F_4. The former type of overlap is generally observed in the TCNQ-F_4 complexes of the [3_n]cyclophanes, and the transannular D-A distance (3.22 Å) is much shorter than that in the latter (3.58 Å). This supports the idea that the methyl-substituted benzene ring interacts more strongly than the methyl-unsubstituted benzene ring with the acceptor. Consistently with this, two types of acceptor columns are observed, and the transannular distances between acceptors are 3.45 Å for the methyl-unsubstituted side and 3.26 Å for the methyl-substituted side. In the 2,11,20-trithia[3_3](1,3,5)cyclophane (**4**)-TCNQ-F_4 (1:1) complex, an alternating D-A stacking similar to that in [3_3](1,3,5)cyclophane (**2**)-TCNQ-F_4 (1:1) is observed. The acceptors are stacked in a parallel fashion and form an infinite column, the A–A distance in the (**4**)-TCNQ-F_4 (1:1) complex being 3.10 Å, and the acceptors in the unit cell are arranged parallel in a plane, the A-A distance being 3.12 Å.

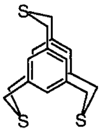
Introduction

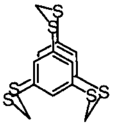
In previous papers we have reported the strong electron-donating abilities of [3_n]cyclophanes (CPs) (n = 3−6), their solid-state structural properties, and structural and electrical properties of their charge-transfer (CT) complexes with acceptors such as TCNQ and TCNQ-F_4.[2,3]


1: $Me_3[3_3]CP$


2: $[3_3]CP$


3: $[3_6]CP$


4: $S_3[3_3]CP$


5: $S_6[3_3]CP$

Among the [3_n]CP-TCNQ-F_4 complexes (n = 3−6), the [3_3](1,3,5)CP **2**-TCNQ-F_4 (1:1) complex showed the highest conductivity in single crystals, and this was ascribed to the formation of an infinite column of partially overlapped acceptors with a short acceptor−acceptor distance and to the close contact of the acceptors arranged parallel in a plane of the unit cell, while no formation of such a column was observed in the TCNQ-F_4 (1:1) complex of the [3_6]CP **3**, irrespective of the strongest donating ability in the [3_n]CPs (n = 2−6).[3a] In the crystal packing diagram of the [3_n]CPs, neighboring cyclophane molecules are arranged in an orthogonal fashion,[3] whereas the 5,7,9-trifluoro- and 5,7,9,14,16,18-hexafluoro[3_3](1,3,5)CPs are stacked with the fluorinated benzene rings facing each other, with the repeated stacking forming a column in the solid state.[4] We have modified the [3_3](1,3,5)CP skeleton in order to study

---

[‡] Multibridged [3_n]cyclophanes, 16. Part 15: Ref.[1]

[a] Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University,
Hakozaki, Fukuoka 812-8581, Japan
Fax: (internat.) + 81-92/642-27354
E-mail: shinmyo@ms.ifoc.kyushu-u.ac.jp

[b] Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812-8581, Japan

[c] Henkel Research Center of Advanced Technology, Molecular Engineering Institute, Kinki University,
Kayanomori 11-6, Iizuka, Fukuoka 820-8555, Japan

[d] Department of Applied Chemistry, Kyushu Institute of Technology,
1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan

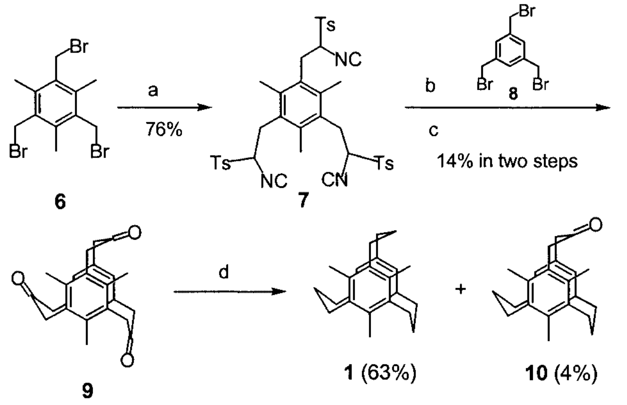
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

the donor (D)−acceptor (A) interaction in the solid state in more detail. We chose 5,7,9-trimethyl[3_3](1,3,5)CP **1** as a donor with two binding sites of different donating ability, as well as 2,11,20-trithia[3_3](1,3,5)CP **4**[5] and 1,3,10,12,19,21-hexathia[3_3](1,3,5)CP **5**[6] as donors with enhanced intermolecular interactions in the crystal packing.

Results and Discussion

Synthesis

The Me_3[3_3](1,3,5)CP **1** was synthesized by the *p*-tolylsulfonylmethyl isocyanide (TosMIC) coupling method.[7−9] The TosMIC adduct **7** was obtained from 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**6**) and TosMIC[10] under phase-transfer conditions (NaOH, $n$$Bu_4NI$, CH_2Cl_2/H_2O) (76%). Coupling of the adduct **7** with 1,3,5-tris(bromomethyl)benzene (**8**) in the presence of NaH in DMF and subsequent acid hydrolysis gave triketone **9** (14%). Reduction of the ketone carbonyl groups afforded **1** (63%), along with Me_3[3_3]CP-one **10** (4%). The yield of the TosMIC coupling was moderate, but this synthetic route provided a straightforward and short approach to **1** (Scheme 1). The use of NaH and DMF[9] in place of NaOH in CH_2Cl_2/H_2O under phase-transfer conditions improved the coupling yield.



Scheme 1. Synthesis of 5,7,9-trimethyl[3_3](1,3,5)cyclophane (**1**); a) TosMIC, NaOH, $n$$Bu_4NI$, CH_2Cl_2/H_2O; b) NaH, DMF, room temp.; c) concd. HCl, CH_2Cl_2; d) $H_2NNH_2{\cdot}H_2O$, KOH, diethylene glycol

The 2,11,20-trithia[3_3](1,3,5)CP **4** was prepared by literature procedures,[5] and 1,3,10,12,19,21-hexathia[3_3]-(1,3,5)CP **5** was obtained by coupling of 1,3,5-trimercaptobenzene and CH_2Br_2 in *t*BuOH under high-dilution conditions.[6] General synthetic methods for thia[3_n]CPs ($n = 2-5$) have already been reported by Vögtle et al.[11]

Electronic Properties

In Me_3[3_3](1,3,5)CP **1** (1st HOMO −8.63 eV, PM3),[12] the donating ability of the methyl-substituted benzene ring would be expected to be much stronger than that of the methyl-unsubstituted benzene ring. In $CHCl_3$ solution, the CT band of the **1**-TCNE complex appears at 632 nm, a significant bathochromic shift from that of the [3_3](1,3,5)CP **2** (1st HOMO −8.88 eV, PM3)-TCNE complex (λ_{max} = 594 nm).[13] This indicates that TCNE interacts more strongly with the methyl-substituted benzene ring than with the methyl-unsubstituted one, and the electron-donating ability of **1** is similar to that of [3_4](1,2,3,5)CP (CT band with TCNE, λ_{max} = 632 nm).[13b]

Compound **1** shows a reversible cyclic voltammogram, the first half-wave oxidation potential ($E_{1/2}$) being +0.73 V (E_{pa} = +1.09 V vs. Fc/Fc$^+$, $Cl_2CHCHCl_2$) (Figure 1), much lower than that of [3_3](1,3,5)CP **2** (+1.31 V) and similar to that of [3_4](1,2,3,5)CP (+0.69 V).[3a] Thus, both the $E_{1/2}$ data and the magnitude of the CT interaction indicate that the donating ability of **1** is similar to that of [3_4](1,2,3,5)CP. S_3[3_3](1,3,5)CP **4** (1st HOMO −9.06 eV, PM3) shows its CT band with TCNE at λ_{max} = 530 nm ($CHCl_3$), while S_6[3_3]CP **5** does not show any CT band with TCNE. This is ascribed to the significantly low lying HOMO level of **5** (−9.16 eV, PM3). PM3 calculations indicate that introduction of sulfur atoms onto the bridges of the [3_3](1,3,5)CP significantly lowers the LUMO level and moderately lowers the HOMO level; the LUMO level of S_3[3_3]CP **4** is −0.51 eV and that of S_6[3_3]CP **5** is −1.39 eV.[12] Compound **5** has the smallest HOMO−LUMO gap and the lowest LUMO level of the [3_3](1,3,5)CPs.

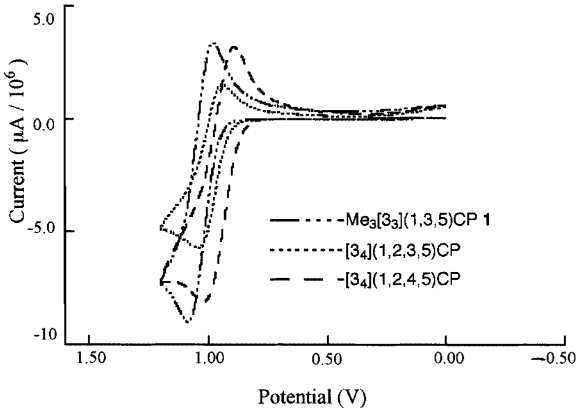
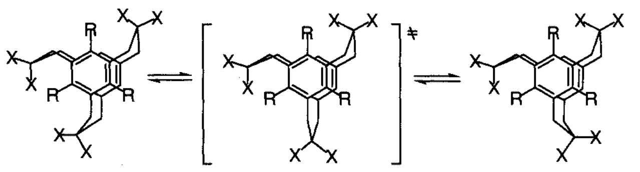


Figure 1. Cyclic voltammograms of [3_n]cyclophanes in $Cl_2CHCHCl_2$ (scan rate 20 mV/s)

Structural Study

In the parent [3_3](1,3,5)CP **2**, two conformers with C_s and C_{3h} symmetries are conceivable, the C_s isomer being more



	R	X
1 (C_s)	CH_3	H
1-[D6] (C_s)	CH_3	D
2 (C_s)	H	H
9 (C_s)	CH_3	C=O
12 (C_s)	H	C=O

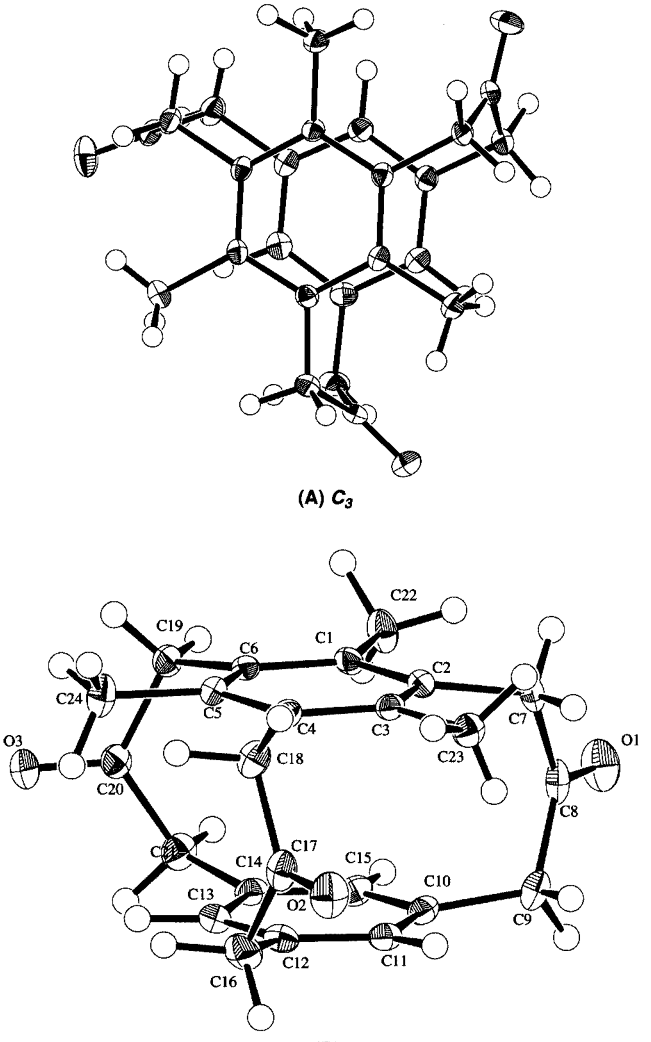
	R	X
1 (TS)	CH_3	H
1-[D6] (TS)	CH_3	D
2 (TS)	H	H
9 (TS)	CH_3	C=O
12 (TS)	H	C=O

	R	X
1 (C_3)	CH_3	H
1-[D6] (C_3)	CH_3	D
2 (C_{3h})	H	H
9 (C_3)	CH_3	C=O
12 (C_{3h})	H	C=O

Scheme 2. Conformational isomerism of [3_3](1,3,5)cyclophanes by a bridge flipping process

stable than the C_{3h} isomer by 0.4 kcal/mol on the basis of a variable temperature (VT) ^{1}H NMR study in CD_2Cl_2. The energy barrier for the bridge flipping process involving **2** (TS) as a transition state is 12.4 kcal/mol (T_c = −70 °C, Scheme 2).[14] The C_s isomer preferred in solution is also observed in the solid state of **2**.[3a] Density functional calculations (B3LYP) on **2** indicate almost the same stability for the two conformers.[15]

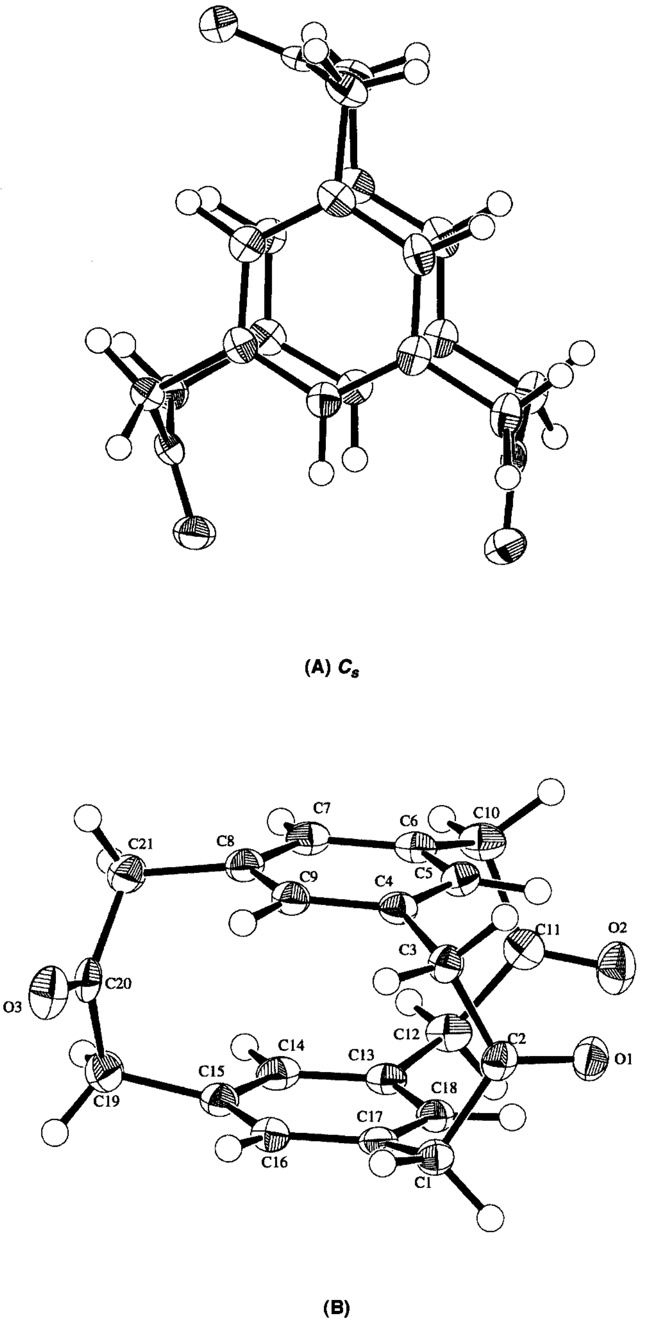
X-ray structural analysis shows that the Me$_3$[3_3](1,3,5)CP-trione **9** has a chiral C_3 symmetry at −170 °C (Figure 2). This is the first example of C_3 or C_{3h} symmetry in the [3_3](1,3,5)CPs; the C_s conformer is generally observed in the crystal structures of [3_3](1,3,5)CPs, as seen in the methyl-unsubstituted trione **12** (Figure 3). Transannular distances between the bridged [3.079(2)−3.083(2) Å] and unbridged carbon atoms [3.137(2)−3.142(2) Å] in **9** are shorter than the corresponding distances in **12** [3.153(3)−3.163(2) Å for the bridged carbon atoms and 3.179(3)−3.231(3) Å for unbridged carbon atoms].



(A) C_3

(B)

Figure 2. ORTEP drawings (A, top view; B, side view) of trimethyl-[3_3](1,3,5)cyclophane-trione (**9**) at −170 °C; selected transannular distances [A]: C(1)−C(15) 3.140(2), C(2)−C(10) 3.079(2), C(3)−C(11) 3.137(2), C(4)−C(12) 3.079(2), C(5)−C(13) 3.142(2), C(6)−C(14) 3.083(2)



(A) C_s

(B)

Figure 3. ORTEP drawings (A, top view; B, side view) of [3_3](1,3,5)cyclophanetrione **12** at −170 °C; selected transannular distances [A]: C(4)−C(17) 3.163(3), C(7)−C(14) 3.179(3), C(5)−C(18) 3.231(3), C(8)−C(15) 3.153(3), C(6)−C(19) 3.156(3), C(9)−C(16) 3.184(3)

The crystal structures (at −170 °C) of Me$_3$[3_3](1,3,5)CP **1** and the monoketone **10** are shown in Figures 4 and 5. Enantiomeric C_3 structures, in which three bridges are directed toward the counterclockwise or clockwise positions, are observed in **1**, as in the case of the trione **9**. The ketone **10** also has a chiral structure with a C_1 symmetry, similar to that of **1**.

We have performed conformational analyses[16] of [3.3]*meta*-[17,18] and [3.3]*para*-cyclophanes,[19,20] and also of

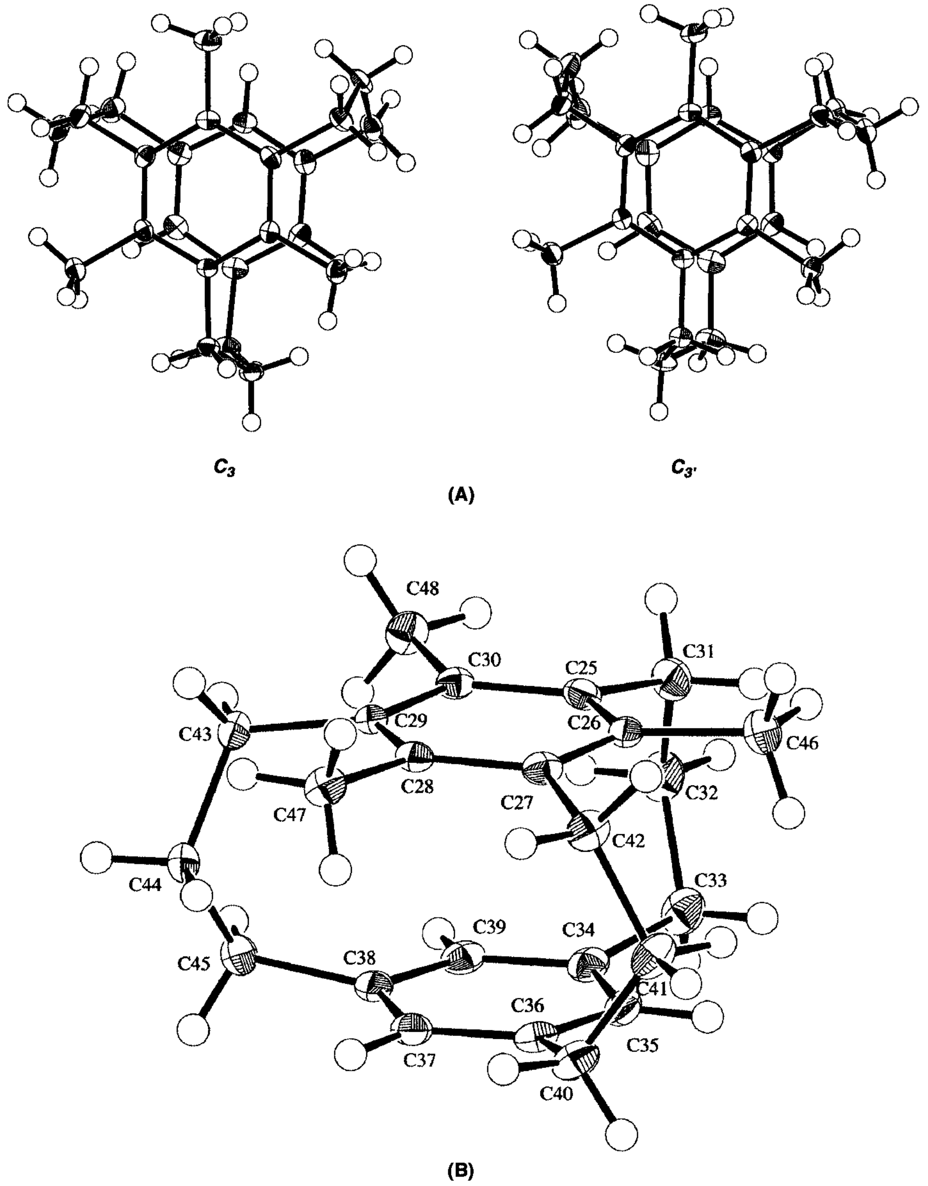


Figure 4. ORTEP drawings (A, top view; B, side view) of trimethyl[3_3](1,3,5)cyclophane (**1**) at −170 °C; selected transannular distances [Å]: C(1)−C(10) 3.072(3), C(2)−C(11) 3.137(4), C(3)−C(12) 3.087(4), C(4)−C(13) 3.173(4), C(5)−C(14) 3.097(4), C(6)−C(15) 3.160(4), C(25)−C(34) 3.090(3), C(26)−C(35) 3.145(3), C(27)−C(36) 3.081(3), C(28)−C(37) 3.158(3), C(29)−C(38) 3.096(3), C(30)−C(39) 3.157(3)

multibridged [3_n]cyclophanes ($n = 3-6$),[14,21,22] by the variable-temperature (VT) ^{1}H and ^{13}C NMR methods. A flipping process of the bridges similar to that in [3_3](1,3,5)CP **2** was observed in the ^{1}H NMR spectrum of **1** in CD_2Cl_2. The aromatic and methyl proton signals appear as singlets at $\delta = 6.78$ and 2.24 ppm at 20 °C, while the benzylic proton signals show strongly temperature-dependent behavior (300 MHz, CD_2Cl_2, Figure S2, Supporting Information; see also footnote on the first page of this article). The benzylic proton signals of **1-[D$_6$]**[23] show two singlets at $\delta = 2.68$ and 2.88 ppm at 20 °C, and each signal gradually broadens as the temperature is lowered, finally splitting into a pair of doublets [$\delta = 2.35$ ppm (d, $J = 13.7$ Hz) and 2.91 (d, $J = 14.0$ Hz); $\delta = 2.73$ ppm (d, $J = 14.7$ Hz) and 2.89 (d, $J = 15.0$ Hz)] at −90 °C (500 MHz, CD_2Cl_2, Figure S3, Supporting Information]. This indicates that the bridge flipping slows down as the temperature is lowered and the molecule is frozen as the preferred C_3 conformer at −90 °C. Similarly, only the C_3 conformer is observed in the ^{13}C NMR spectrum of **1** at −91 °C.[24] The energy barrier for this process, based on the benzylic proton signals of **1**, is estimated as 9.9 ± 0.2[25,26] and 10.4 ± 0.2 [27] kcal/mol ($T_c = -48$ °C). Compound **1** therefore exists as the C_3 conformer both in solution and in the solid state, and this is in sharp contrast with the parent **2**. The ^{1}H NMR spectrum of the Me$_3$[3_3]CP-trione **9** shows aromatic and methyl proton signals as singlets at $\delta = 7.00$ and 2.33 ppm, while both benzylic proton signals also appear as singlets at $\delta = 3.66$

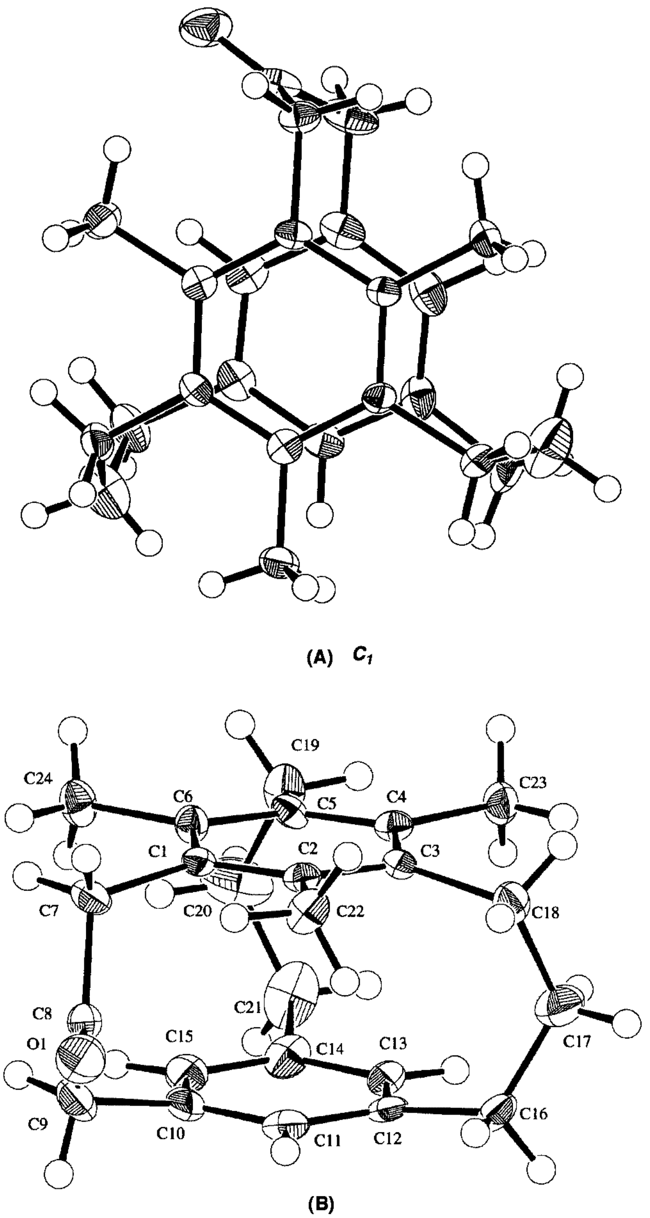


Figure 5. ORTEP drawings (A, top view; B, side view) of trimethyl-[3$_3$](1,3,5)cyclophane-2-one (**10**) at −170 °C; selected transannular distances [Å]: C(1)−C(10) 3.099(8), C(2)−C(11) 3.154(8), C(3)−C(12) 3.084(8), C(4)−C(13) 3.170(8), C(5)−C(14) 3.093(7), C(6)−C(15) 3.170(8)

and 3.88 ppm in $CDCl_3$. This compound, and also the triketone **12**, show no temperature-dependent phenomena down to −90 °C in their ^1H NMR spectra, suggesting much lower energy barriers to the CH_2COCH_2 bridge flipping process than to the $CH_2CH_2CH_2$ bridge flipping process.

Solid-State Structures of the CT Complexes[3,28]

Two types of D-A overlap are observed in the crystals of **1**-TCNQ-F_4 (1:1) complex at −170 °C (Figure 6). One is partial D-A overlap of the methyl-substituted benzene ring and TCNQ-F_4, generally observed in TCNQ-F_4 complexes of [3$_3$](1,3,5)CP **2**[3a] and [3$_6$]CP **3**,[2][3a] and ascribed to efficient HOMO−LUMO orbital interactions. In contrast, nearly complete D-A overlap is observed between the methyl-unsubstituted benzene ring and TCNQ-F_4. The former transannular D-A distance (3.22 Å) is much shorter than that for the methyl-unsubstituted benzene ring and TCNQ-F_4 (3.58 Å), which clearly supports the idea that the methyl-substituted benzene ring interacts more strongly than the methyl-unsubstituted benzene ring with the acceptor. The donors and acceptors are stacked alternately as usual.[2,3] Two types of acceptor columns are observed, and the transannular distances between acceptors are 3.45 Å on the methyl-unsubstituted side and 3.26 Å on the methyl-substituted side (Figure 7).

The cyclophane moiety in the S_3[3$_3$](1,3,5)CP **4**-TCNQ-F_4 (1:1) complex shows a C_s structure in the crystals at −170 °C, as in the case of the free cyclophane **4**.[29] The transannular D-A distance is 3.29 Å and the average transannular distance between two benzene rings is 3.23 Å. The overlapping mode of the donor and acceptor is similar to that in [3$_3$]CP **2**-TCNQ-F_4 (Figure 8).[3] An alternating D-A stacking similar to that of **2**-TCNQ-F_4 is observed in the crystal packing diagram. The partially overlapped acceptors form an infinite column with distances of 3.10 Å between acceptors [Figure 9 (A)], a distance longer than that in the [3$_3$]CP **2**-TCNQ-F_4 (1:1) complex (2.93 Å), probably because of the weaker donating ability of **4** than of **2**. Close contact between the acceptors (3.12 Å) arranged parallel in a plane of the unit cell is also observed [Figure 9 (B)], as in the case of the crystal packing of [3$_3$](1,3,5)CP **2**-TCNQ-F_4 (1:1) complex.[3a]

Conclusion

Me_3[3$_3$](1,3,5)CP **1** adopts the C_3 conformation both in the solid state (−170 °C) and in solution (CD_2Cl_2, −90 °C). The same conformation is observed in the triketone **9** in the solid state, and the result is in sharp contrast with the preferred C_s conformers of the parents **2** and **12**. The electron-donating ability of **1**, from the magnitude of the CT interaction and the oxidation potential ($E_{1/2}$), is similar to that of [3$_4$](1,2,3,5)CP. In the Me_3[3$_3$]CP **1**-TCNQ-F_4 (1:1) complex, the methyl-substituted benzene ring interacts more strongly than the methyl-unsubstituted one with the acceptor. The D-A stacking mode in the S_3[3$_3$](1,3,5)CP **4**-TCNQ-F_4 (1:1) complex is similar to that in the [3$_3$]CP **2**-TCNQ-F_4 (1:1) complex, and the fact that the A−A distances in an acceptor column are longer in the former than in the latter reflect the weaker donating ability of **4** relative to **2**. The expected intermolecular interaction of the sulfur atoms in the solid state is not observed in the S_3[3$_3$](1,3,5)CP **4**-TCNQ-F_4 (1:1) complex. Thus, modest modification of the skeleton of the donor effects changes in the D-A overlapping mode and the crystal packing mode. Single-crystal conductivity data for the **1**- and **4**-TCNQ-F_4 (1:1) complexes have not yet been obtained because of insufficient amounts of the single crystals.

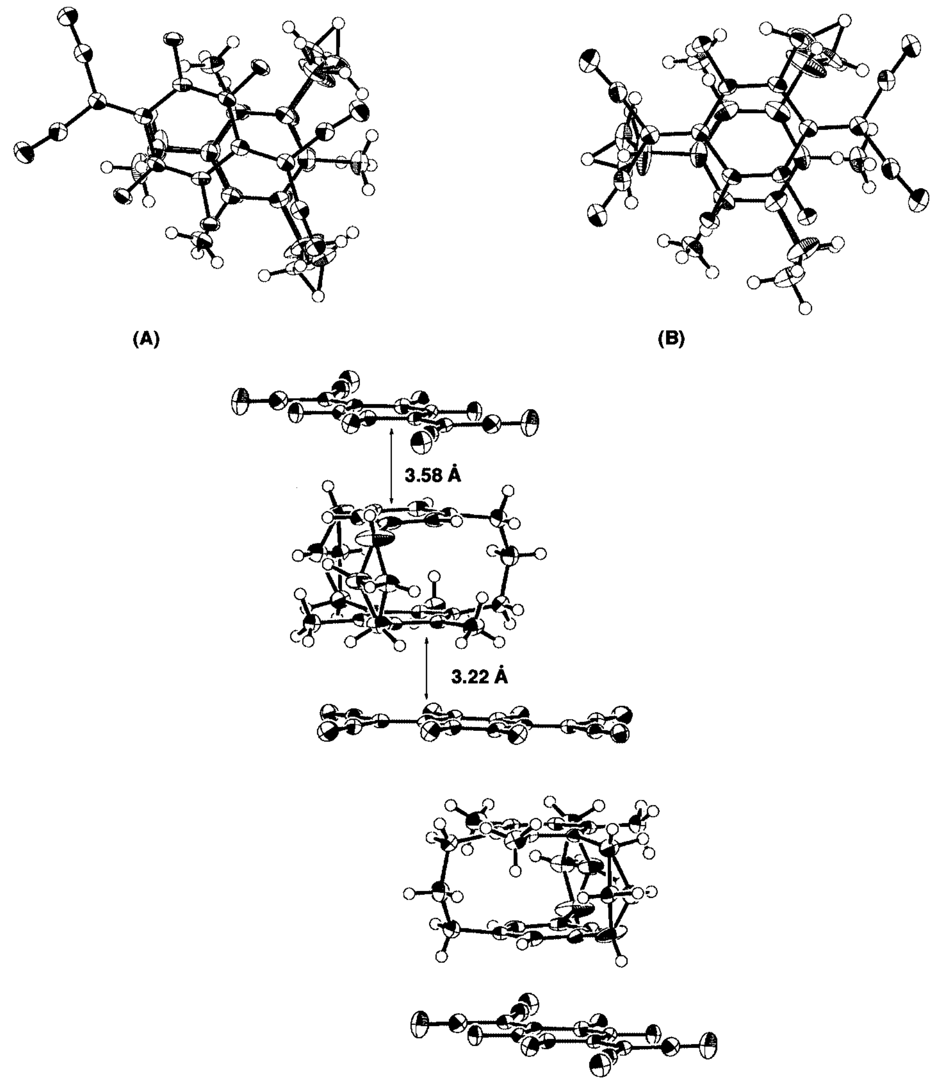


Figure 6. The crystal structure of the trimethyl[3_3](1,3,5)cyclophane (**1**)-TCNQ-F_4 (1:1) complex at −170 °C: side views (A and B) and top view (C)

Experimental Section

General: Melting points: Yanako micro melting point apparatus MP-S3. NMR: JEOL JNM-GX 270, AL-300, and A500. Chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane (TMS) in $CDCl_3$ unless otherwise noted. FAB-MS: JEOL JMS-SX/SX 102A mass spectrometer (*m*-nitrobenzyl alcohol). IR: Hitachi Nicolet I-5040 FT-IR. Elemental analysis: The Service Center for the Elementary Analysis of Organic Compounds, affiliated to the Faculty of Science, Kyushu University. Analytical thin layer chromatography (TLC) and column chromatography were performed on 60 F_{254} silica gel (Merck) and silica gel 60 (40−63 μm), respectively. DMF was dried with molecular sieves (4 Å). 2,11,20-Trithia[3_3](1,3,5)cyclophane (**4**) was obtained by treatment of 1,3,5-tris(bromomethyl)benzene with Na_2S/Al_2O_3 in CH_2Cl_2/EtOH.[5b] 1,3,10,12,19,21-Hexathia[3_3](1,3,5)cyclophane (**5**) was prepared by means of the coupling reaction between 1,3,5-trimercaptobenzene[30] and CH_2Br_2 in *t*BuOH under high-dilution conditions (10%).[6] 2,4,6-Tris(bromomethyl)-1,3,5-trimethylbenzene (**6**) was prepared by bromomethylation of 1,3,5-trimethylbenzene by the procedures reported by Van der Made et al.[31] Cyclic voltammograms were recorded with a BAS-100 B/W electrochemical analyzer. A Pt wire counter-electrode and an Ag/0.01 M $AgNO_3$ reference electrode were used. The measurements were carried out in a 0.1 M 1,1,2,2-tetrachloroethane solution of a substrate with Bu_4NPF_6 as supporting electrolyte, and the oxidation potential values were calibrated with ferrocene. 1,1,2,2-Tetrachloroethane was dried with $CaCl_2$ and distilled just before use.

X-ray Crystallographic Study: All measurements were made with a Rigaku RAXIS-RAPID-S imaging plate area detector with graphite-monochromated Mo-K_α (λ = 0.71069 Å) and Cu-K_α (λ = 1.54178 Å) radiation and a rotating anode generator. The crystal structures were solved by direct methods [SIR92[32] (**1**, **9**, **10**, **4**-TCNQ-F_4, **1**-TCNQ-F_4), MULTAN88[33] (**12**) and expanded by use of Fourier techniques (DIRDIF94[34]). The non-hydrogen atoms were refined anisotropically (**1**, **9**, **10**, **12**, **4**-TCNQ-F_4) and refined by full-matrix least squares (**1**-TCNQ-F_4),[35] while hydrogen atoms were refined isotropically. All the computations were performed by use of teXsan.[36] CCDC-184791 (**1**), -184794 (**9**), -184793 (**10**), -184790 (**12**), -184792 (**1**-TCNQ-F_4), and -184795 (**4**-TCNQ-F_4)

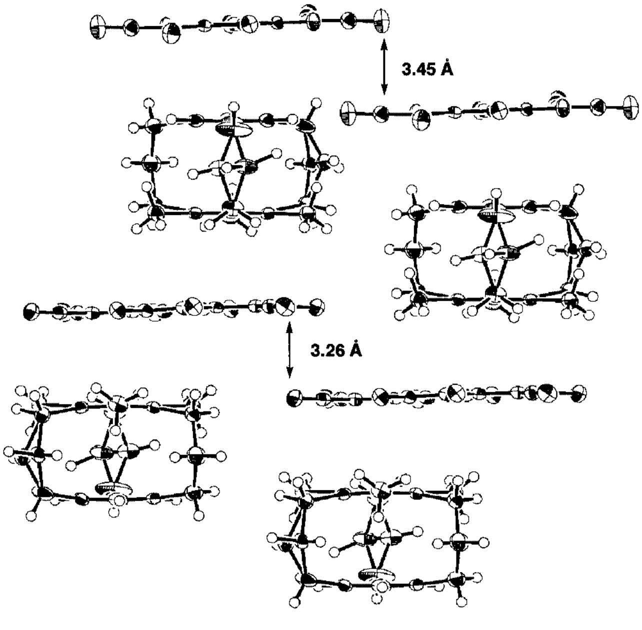


Figure 7. The crystal packing diagram of the trimethyl[3$_3$](1,3,5)-cyclophane (**1**)-TCNQ-F$_4$ (1:1) complex at −170 °C

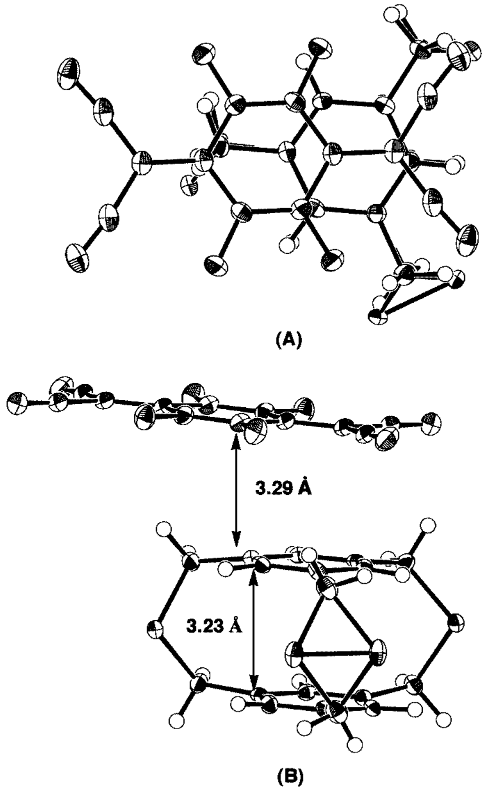


Figure 8. The crystal structure of the trithia[3$_3$](1,3,5)cyclophane **4**-TCNQ-F$_4$ (1:1) complex at −170 °C (A, top view; B, side view)

contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

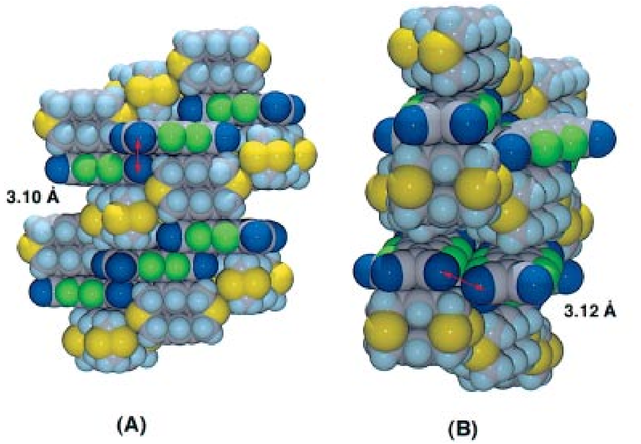


Figure 9. ORTEP drawings (CPK model) of the crystal packing diagram of trithia[3$_3$](1,3,5)cyclophane **4**-TCNQ-F$_4$ (1:1) complex at −170 °C

1,3,5-Tris[2-isocyano-2-(tolylsulfonyl)ethyl]-2,4,6-trimethylbenzene (7): TosMIC (15.0 g, 76.8 mmol) in CH_2Cl_2 (60 mL) was added dropwise at 0−10 °C over a period of 1 h to a stirred mixture of NaOH (15.0 g, 375 mmol) and nBu$_4$NI (1.0 g) in water (25 mL) and CH_2Cl_2 (50 mL). After the addition, 2,4,6-tris(bromomethyl)-1,3,5-trimethylbenzene (**6**, 6.81 g, 17.1 mmol) in CH_2Cl_2 (70 mL) was added to the mixture at 0−10 °C over 10 min. After the addition, the mixture was stirred overnight. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the concentrate was diluted with CH_2Cl_2/MeOH (1:5). The resulting precipitate was collected by filtration to give the TosMIC adduct **7** (9.62 g, 76%). Orange powder reprecipitated from CH_2Cl_2/MeOH (1:5), m.p. 178−179 °C (dec.). ^{1}H NMR: $\delta = 2.21$ (s, 3 H, $-CH_3$), 2.31 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.50 (s, 9 H, CH_3), 3.50 (m, 6 H, $C\mathit{H_2}CH$), 4.52 (m, 3 H, $CH_2C\mathit{H}$), 7.43−7.45 (m, 6 H, ArH), 7.88−7.91 (m, 6 H, ArH) ppm. IR (KBr): $\tilde{\nu} = 2135$ (NC) cm^{-1}. FABMS: $m/z = 742$ [M$^+$ + 1]. $C_{39}H_{39}N_3O_6S_3$ (742): calcd. C 63.13, H 5.30, N 5.66; found C 63.21, H 5.45, N 5.84.

5,7,9-Trimethyl[3$_3$](1,3,5)cyclophane-2,11,20-trione (9): A mixture of 1,3,5-tris(bromomethyl)benzene (**8**, 3.85 g, 10.8 mmol) and **7** (8.00 g, 10.8 mmol) in DMF (1.0 L) was added dropwise at room temperature over a period of 10 h to a stirred suspension of NaH (60%, 1.55 g, 38.8 mmol) in DMF (1500 mL). After completion of addition, the mixture was stirred overnight. The DMF was removed under reduced pressure and water was added to the residue. The mixture was extracted with CH_2Cl_2. HCl (concd., 200 mL) was added to the combined extracts, and the mixture was stirred overnight at room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The organic portion and CH_2Cl_2 extracts were combined, and the combined CH_2Cl_2 solutions were washed with brine, dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the concentrate was diluted with MeOH to give the triketone **9** (550 mg, 14%). Colorless prisms [CH_2Cl_2/hexane (3:1)], m.p. > 300 °C. ^{1}H NMR: $\delta = 2.33$ (s, 9 H, CH_3), 3.66 (s, 6 H, $CH_2COC\mathit{H_2}$), 3.88 (s, 6 H, $C\mathit{H_2}COCH$), 7.00 (s, 3 H, ArH) ppm. IR (KBr): $\tilde{\nu} = 1687$ (C=O) cm^{-1}. FABMS: $m/z = 360$ [M$^+$]. $C_{24}H_{24}O_3$ (360): calcd. C 79.97, H 6.71; found C 79.93, H 6.71.

5,7,9-Trimethyl[3$_3$](1,3,5)cyclophane (1): A mixture of **9** (246 mg, 0.682 mmol), KOH (3.0 g), triethylene glycol (70 mL), and

Table 1. Summary of crystallographic data and refinement details

	9	**12**	**1**	**10**	**1**-TCNQ-F$_4$	**4**-TCNQ-F$_4$
Empirical formula	$C_{24}H_{24}O_3$	$C_{21}H_{18}O_3$	$C_{24}H_{30}$	$C_{24}H_{28}O$	$C_{36}H_{30}F_4N_4$	$C_{30}H_{18}F_4N_4S_3$
Formula mass	360.45	318.37	318.5	332.48	594.65	606.67
Crystal color and habit	yellow prism	colorless prism	colorless prism	colorless prism	black prism	black prism
Crystal size [mm]	0.50 × 0.15 × 0.50	0.30 × 0.20 × 0.10	0.50 × 0.20 × 0.10	0.30 × 0.10 × 0.50	0.25 × 0.05 × 0.30	0.40 × 0.05 × 0.35
Crystal system	monoclinic	monoclinic	orthorhombic	tetragonal	triclinic	monoclinic
Space group	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$Pbca$ (no.61)	$P4_2bc$ (no.106)	$P\bar{1}$ (no.2)	$C2/c$ (no.15)
Temperature [°C]	−170	−170	−170	−170	−150	−170
a [Å]	9.2787(2)	13.689(1)	27.9768(5)	19.7229(8)	9.2797(3)	25.7978(8)
b [Å]	9.8357(3)	8.3921(7)	26.3687(6)	19.7229(8)	9.8998(3)	8.4535(4)
c [Å]	19.6689(5)	14.933(1)	9.5405(2)	8.9812(3)	17.6269(4)	14.5992(5)
α [°]					82.786(1)	
β [°]	100.7094(5)	115.820(2)			100.1819(9)	123.7236(8)
γ [°]					117.553(9)	
V [Å^3]	1763.78(7)	1544.2(2)	7038.1(4)	3493.6(2)	1411.28(7)	2648.1(2)
Z	4.0	4.0	16.0	8.0	2.0	4.0
$\rho_{calcd.}$ [g/cm^3]	1.357	1.369	1.202	1.264	1.399	1.522
$F(000)$	768.00	672.00	2784.00	1440.00	620.00	1240.00
μ [cm^{-1}]	0.88 (Mo-K_α)	0.91 (Mo-K_α)	0.67 (Mo-K_α)	0.75 (Mo-K_α)	8.42 (Cu-K_α)	3.38 (Mo-K_α)
$2\theta_{max}$ [°]	55.0 ($I > 3.0\sigma$)	55.0 ($I > 3.0\sigma$)	55.0 ($I > 3.0\sigma$)	55.0 ($I > 3.0\sigma$)	136.5 ($I > 2.0\sigma$)	55.0 ($I > 3.0\sigma$)
No. of reflections	16276	9917	54897	27642	4834	11718
Measured reflections	4033	3425	8036	2139	4834	3014
R_{int}	0.030	0.081	0.052	0.072	0.050	0.032
Observed reflections	3169	2246	4585	1582	3763	1911
No. of parameters	341	290	434	227	419	191
Reflection/parameter ratio	9.29	7.74	10.56	6.97	8.98	10.01
R	0.046	0.055	0.052	0.070	0.056	0.039
Rw	0.076	0.081	0.075	0.105	0.157	0.052
GOF	1.27	1.30	1.22	1.30	1.09	1.21

$NH_2NH_2{\cdot}H_2O$ (15 mL) was heated at 130 °C for 3.5 h while stirring and then at 200 °C for 2 h. The reaction mixture was poured into a mixture of ice/water and concd. HCl, and the mixture was extracted with *tert*-butyl methyl ether. The combined extracts were washed with water, dried with Na_2SO_4, and filtered. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2/hexane (1:3) to give **1** (137 mg, 63%, $R_f = 0.50$), along with 5,7,9-trimethyl[3$_3$](1,3,5)cyclophane-2-one (**10**, 8 mg, 4%). **1**: Colorless prisms (hexane), m.p. 225−226 °C. ^{1}H NMR: δ = 2.07−2.15 (m, 6 H, $CH_2CH_2CH_2$), 2.24 (s, 9 H, CH_3), 2.68 (t, J = 6.1 Hz, 4 H, $CH_2CH_2CH_2$), 2.88 (t, J = 6.2 Hz, 4 H, $CH_2CH_2CH_2$), 6.84 (s, 3 H, ArH) ppm. FABMS: m/z = 318 [M$^+$]. $C_{24}H_{30}$ (318): calcd. C 90.51, H 9.49; found C 90.29, H 9.40. **10:** Colorless prisms (CH_2Cl_2/hexane), m.p. 232−233 °C. ^{1}H NMR: δ = 2.12−2.16 (m, 4 H, $CH_2CH_2CH_2$), 2.27 (s, 9 H, CH_3), 2.67−2.72 (m, 4 H, $CH_2CH_2CH_2$), 2.91 (t, J = 6.3 Hz, 4 H, $CH_2CH_2CH_2$), 3.62 (s, 2 H, CH_2COCH_2), 3.80 (s, 2 H, CH_2COCH_2), 6.84 (s, 3 H, ArH) ppm. IR (KBr): $\tilde{\nu}$ = 1688 (C=O) cm^{-1}. FABMS: m/z = 332 [M$^+$]. $C_{24}H_{28}O$ (332): calcd. C 86.70, H 8.49; found C 86.35, H 8.38.

CT Complexes: TCNQ-F$_4$ (12.4 mg, 0.045 mmol) was dissolved in $CHCl_3$ (13 mL) in a 100-mL glass vial at room temperature, and this solution was mixed with Me$_3$[3$_3$]CP **1** (14.3 mg, 0.045 mmol) in $CHCl_3$ (10 mL). The mixture was allowed to stand until blue crystals of the Me$_3$[3$_3$]CP **1**-TCNQ-F$_4$ (1:1) complex were formed. IR (KBr): $\tilde{\nu}$ = 2223 (CN) cm^{-1}. Similarly, the S$_3$[3$_3$]CP **4**-TCNQ-F$_4$ (1:1) complex was obtained as dark-red prisms by recrystallization from a mixture of $CHCl_3$ and CH_3CN (1:1). IR (KBr): $\tilde{\nu}$ = 2217 (CN) cm^{-1}.

Acknowledgments

We gratefully acknowledge financial support by a Grant-in-Aid for Scientific Research (B) (No. 14340200) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. T. S. sincerely thanks for the financial support by the Shorai Foundation for Science and Technology, Japan.

---

[1] W. Matsuda-Sentou, T. Shinmyozu, *Tetrahedron: Asymmetry* **2001**, *12*, 839−842.

[2] M. Yasutake, Y. Sakamoto, S. Onaka, K. Sako, H. Tatemitsu, T. Shinmyozu, *Tetrahedron Lett.* **2000**, *41*, 7933−7938.

[3] [3a] M. Yasutake, T. Koga, Y. Sakamoto, S. Komatsu, M. Zhou, K. Sako, H. Tatemitsu, S. Onaka, Y. Aso, S. Inoue, T. Shinmyozu, *J. Am. Chem. Soc.* **2002**, *124*, 10136−10145. [3b] M. Yasutake, T. Koga, C. Lim, M. Zhou, W. Matsuda-Sentou, T. Shinmyozu, in *Cyclophane Chemistry for the 21st Century* (Ed.: H. Takemura), Research Signpost, Kerana, India, **2002**, p. 265−300.

[4] T. Koga, M. Yasutake, T. Shinmyozu, *Org. Lett.* **2001**, *3*, 1419−1422.

[5] [5a] F. Vögtle, *Justus Liebigs Ann. Chem.* **1970**, *735*, 193−195. [5b] R. G. Lichtenthaler, F. Vögtle, *Chem. Ber.* **1973**, *106*, 1319−1327.

[6] F. Vögtle, R. G. Lichtenthaler, *Tetrahedron Lett.* **1972**, 1905−1906.

[7] [7a] K. Kurosawa, M. Suenaga, T. Inazu, T. Yoshino, *Tetrahedron Lett.* **1982**, *23*, 5335−5338. [7b] T. Shinmyozu, Y. Hirai, T. Inazu, *J. Org. Chem.* **1986**, *51*, 1551−1555.

[8] H. Sasaki, T. Kitagawa, *Chem. Pharm. Bull.* **1983**, *31*, 2868−2878.

[9] J. Breitenbach, F. Vögtle, *Synthesis* **1992**, 41−42.

[10] [10a] B. E. Hoogenboom, O. H. Oldenziel, A. M. van Leusen, *Org. Synth.* **1977**, *57*, 102−106. [10b] A. M. van Leusen, R. J. Bouma, O. Possel, *Tetrahedron Lett.* **1975**, *16*, 3487−3488.

[11] F. Vögtle, *Chem.-Ztg.* **1971**, *95*, 668−669.

[12] The semiempirical MO calculations were performed with the aid of the MOPAC2000 programs, graphically facilitated by use of WINMOPAC ver. 3 (Fujitsu Limited).

[13] [13a] Y. Sakamoto, N. Miyoshi, T. Shinmyozu, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 549−550. [13b] Y. Sakamoto, N. Miyoshi, M. Hirakida, S. Kusumoto, H. Kawase, J. M. Rudzinski, T. Shinmyozu, *J. Am. Chem. Soc.* **1996**, *118*, 12267−12275. [13c] T. Shinmyozu, M. Hirakida, S. Kusumoto, M. Tomonou, T. Inazu, J. M. Rudzinski, *Chem. Lett.* **1994**, 669−672. [13d] Y. Sakamoto, T. Shinmyozu, *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2*, 371−399.

[14] T. Meno, K. Sako, M. Suenaga, M. Mouri, T. Shinmyozu, T. Inazu, H. Takemura, *Can. J. Chem.* **1990**, *68*, 440−445.

[15] K. Hori, W. Sentou, T. Shinmyozu, *Tetrahedron Lett.* **1997**, *38*, 8955−8958.

[16] For a very recent review on conformational study of cyclophanes, see: L. Ernst, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *37*, 47−190.

[17] [17a] K. Sako, T. Hirakawa, N. Fujimoto, T. Shinmyozu, T. Inazu, H. Horimoto, *Tetrahedron Lett.* **1988**, *29*, 6275−6278. [17b] K. Sako, T. Shinmyozu, H. Takemura, M. Suenaga, T. Inazu, *J. Org. Chem.* **1992**, *57*, 6536−6541. [17c] T. Shinmyozu, T. Hirakawa, G. Wen, S. Osada, H. Takemura, K. Sako, J. M. Rudzinski, *Liebigs Ann.* **1996**, 205−210. [17d] H. Takemura, H. Kariyazono, M. Yasutake, N. Kon, K. Tani, K. Sako, T. Shinmyozu, T. Inazu, *J. Org. Chem.* **1999**, *64*, 9077−9079. [17e] G. Wen, W. Matsuda-Sentou, K. Sameshima, M. Yasutake, D. Noda, C. Lim, T. Satou, H. Takemura, K. Sako, H. Tatemitsu, T. Inazu, T. Shinmyozu, *J. Am. Chem. Soc.*, in press. [17f]T. Satou, T. Shinmyozu, *J. Chem. Soc., Perkin Trans. 2.* **2002**, 393−397.

[18] M. F. Semmelhack, J. J. Harrison, D. C. Young, A. Gutiérrez, S. Rafii, J. J. Clardy, *J. Am. Chem. Soc.* **1985**, *107*, 7508−7514.

[19] F. A. L. Anet, M. A. Brown, *J. Am. Chem. Soc.* **1969**, *91*, 2389−2391.

[20] K. Sako, T. Meno, H. Takemura, T. Shinmyozu, T. Inazu, *Chem. Ber.* **1990**, *123*, 639−642.

[21] [21a] T. Shinmyozu, M. Hirakida, S. Kusumoto, M. Tomonou, T. Inazu, J. M. Rudzinski, *Chem. Lett.* **1994**, 669−672. [21b] K. Hori, W. Sentou, T. Shinmyozu, *Tetrahedron Lett.* **1997**, *38*, 8955−8958. [21c] Y. Sakamoto, N. Miyoshi, M. Hirakida, S. Kusumoto, H. Kawase, J. M. Rudzinski, T. Shinmyozu, *J. Am. Chem. Soc.* **1996**, *118*, 12267−12275. [21d] Y. Sakamoto, T. Shinmyozu, *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2*, 371−399.

[22] H. F. Bettinger, P. v. R. Schleyer, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1998**, *120*, 1074−1075.

[23] Hexadeuterated Me$_3$[3_3](1,3,5)CP **1-[D$_6$]** was prepared from the triketone **9** via the thioacetal, followed by nBu$_3$SnD reduction in refluxing xylene.[17b]

[24] The ^{13}C NMR spectroscopic data of the Me$_3$[3_3]CP **1** at −91 °C (CD$_2$Cl$_2$, 75 MHz) support the C_3 symmetry of the conformer because four aliphatic carbon atoms (δ = 19.3, 25.3, 29.4, and 35.5 ppm) and four aromatic carbon signals (δ = 124.8, 133.4, 135.8, 141.4 ppm) are observed.

[25] [25a] A. Mannschreck, G. Rissmann, F. Vögtle, D. Wild, *Chem. Ber.* **1967**, *100*, 335−346. [25b] I. C. Calder, P. J. Garratt, *J. Chem. Soc. B* **1967**, 660−662. $\Delta G^{\ddagger}$ [cal/mol] = $2.303 \times 1.987\, T_c\, (10.319 - \log_{10}\kappa_c + \log_{10}T_c)$ where $\kappa_c = \pi\, 2^{1/2}[(\nu_A - \nu_B)^2 + 6\, J_{AB}^2)^{1/2}$.

[26] $\Delta G^{\ddagger} = 9.9$ kcal/mol: $\Delta\nu = \nu_A - \nu_B = 280$, $J_{AB} = 13.8$ Hz, $T_c = -48$ °C.

[27] $\Delta G^{\ddagger} = 10.4$ kcal/mol: $\Delta\nu = \nu_A - \nu_B = 80$, $J_{AB} = 14.8$ Hz, $T_c = -48$ °C.

[28] [28a] C. Cohen-Addad, M. Lebars, A. Renault, P. Baret, *Acta Crystallogr., Sect. C* **1984**, *40*, 1927−1931. [28b] A. Renault, C. Cohen-Addad, *Acta Crystallogr., Sect. C* **1986**, *42*, 1529−1533. [28c] A. Renault, C. Cohen-Addad, J. Lajzerowicz-Bonneteau, J-P. Dutasta, M. J. Crisp, *Acta Crystallogr., Sect. B* **1987**, *43*, 480−488. [28d] A. Renault, C. Cohen-Addad, P. Baret, *Stud. Phys. Theor. Chem.* **1987**, *46*, 611−612. [28e] A. Renault, C. Cohen-Addad, J. Lajzerowicz, E. Canadell, O. Eisenstein, *Mol. Cryst. Liq. Cryst.* **1988**, *164*, 179−195.

[29] A. W. Hanson, E. W. Macaulay, *Acta Crystallogr., Sect. B* **1972**, *28*, 1255−1260.

[30] [30a] R. Adams, A. Ferretti, *J. Am. Chem. Soc.* **1959**, *81*, 4927−4931. [30b] R. Adams, A. Ferretti, *J. Am. Chem. Soc.* **1959**, *81*, 4939−4940.

[31] A. W. Van der Made, R. H. Van der Made, *J. Org. Chem.* **1993**, *58*, 1262−1263.

[32] *SIR92:* A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[33] *MULTAN88:* T. Debaerdemaeker, G. Germain, P. Main, L. S. Refaat, C. Tate, M. M. Woolfson, *Computer programs for the automatic solution of crystal structures from X-ray diffraction data*, University of York, U.K., **1988**.

[34] *DIRDIF94:* P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-94 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.

[35] *SHELXL-97:* G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[36] *teXsan:* Crystal Structure Analysis Package, Molecular Structure Corporation, **1985**, **1999**.

Received March 21, 2002
[O02260]