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Crystal structural properties of a pinwheel compound: $[3_6](1,2,3,4,5,6)$cyclophane[†]

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Abstract

In the crystal structures of $[3_6](1,2,3,4,5,6)$cyclophane **1** and the **1**:TCNQ (1:1) complex, the cyclophane moiety is observed as the D_{6h} structure because of the disorder of the molecules with C_{6h} symmetry. In contrast, the C_{6h} structure is observed in the crystals of the **1**:TCNQ-F_4 (1:1) complex, and the complex shows an alternating donor–acceptor stacking with partial donor–acceptor overlap. © 2000 Elsevier Science Ltd. All rights reserved.

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In previous papers, we have reported the synthesis and conformational behavior of a pinwheel molecule with six blades, $[3_6](1,2,3,4,5,6)$cyclophane **1**.[1] The variable temperature ^{1}H NMR study of **1** in toluene-d_8 indicates the rapid flipping of the six bridges at room temperature, and the molecule is frozen to a C_{6h} conformer below ca. −70°C.[1b] The barrier for the flipping process between two degenerate C_{6h} conformers is 10.9 kcal/mol. Ab initio MO calculations also predict the C_{6h} conformer as the most stable structure.[2,3] Our group[2] and Schleyer et al.[3] independently proposed a stepwise flipping process, where the trimethylene bridge changes their conformation step-by-step via several intermediates (Scheme 1). An alternative synchronous mechanism involving a D_{6h} symmetric structure as a transition state is ruled out by its high energy (43.5 kcal/mol)[3] above **1** (C_{6h}). Thus, the structural properties of **1** in solution have been elucidated,

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[†] Multibridged $[3_n]$cyclophanes. Part 12.

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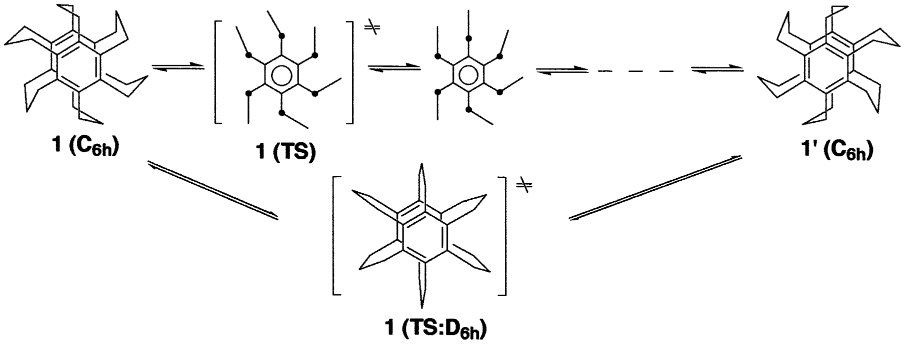
but its fundamental structural parameters have not been reported yet because of the difficulty of its X-ray structural analysis mainly due to the highly symmetrical C_{6h} structure. We describe here the first crystal structural study of **1** and its charge transfer (CT) complexes with TCNQ and TCNQ-F$_4$.[4]



Scheme 1. Two types of inversion mechanisms of the six bridges between degenerate **1**(C_{6h}) and **1**′(C_{6h}): a stepwise flipping mechanism and a synchronous mechanism involving a D_{6h} symmetric structure as a transition state

In the crystal structure of the **1**–TCNQ–benzene (1:1:1) complex at −190°C, a cyclophane (donor) and a TCNQ (acceptor) are stacked with the D–A distance being ca. 3.30 Å. The benzene ring of the cyclophane and the six-membered ring of the TCNQ partially overlap. 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. The short distance (2.64 Å) between an olefinic proton of the TCNQ and a benzene ring suggests the presence of a CH-π interaction (Fig. 1). The cyclophane moiety is observed as a D_{6h} conformer as is the case of free **1** (−180°C, Fig. 2(A)) because of the disorder of molecules with a C_{6h} symmetry. The two neighboring cyclophane molecules face in an orthogonal position in the crystals of free **1**, and this arrangement is generally observed in the crystal structures of [3$_n$]cyclophanes (Fig. 2(B)).[5,6]

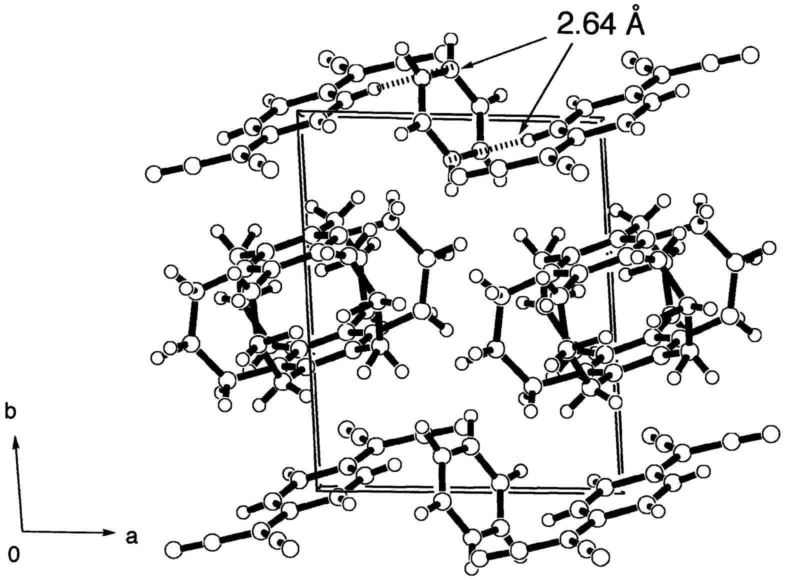


Figure 1. The packing of the molecules in the crystal structure of the **1**–TCNQ–benzene (1:1:1) complex at −190°C

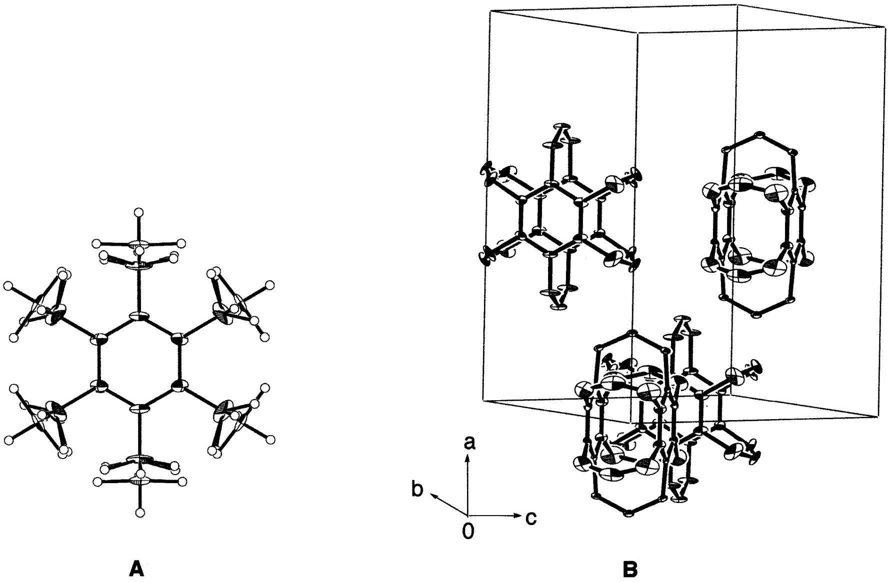


Figure 2. The crystal structure of **1** at −180°C: molecular structure (A) and packing of the molecules (B) (hydrogen atoms are omitted for clarity)

In contrast, the cyclophane moiety of the **1**–TCNQ-F_4 (1:1) complex takes the C_{6h} structure in the crystals (Fig. 3). The transannular D–A distance is 3.22 Å and the average transannular distance between two benzene rings is 2.93 Å (Fig. 4(A)). The overlapping mode of the donor and acceptor is similar to that of **1**–TCNQ (Fig. 4(B)), and this characteristic partial D–A overlap is interpreted by the orbital interactions of the LUMO of the acceptor and the HOMO of the donor (Fig. 4(C)). A similar alternating D–A stacking to that of **1**–TCNQ is observed in the crystal packing diagram (Fig. 4(D)). Although comparison of the bond lengths between experimental data of the complexed **1** and theoretically predicted data of free **1** should be made carefully, the experimental bond lengths of the benzene rings (1.406–1.415 Å) are comparable to those estimated by ab initio MO calculations of **1** (1.414 (B3LYP/DZP)[3] and 1.400 Å (RHF/6-31G)[2]). Similarly, the C_{aromatic}–$C_{\text{aliphatic}}$ (1.520–1.521 Å) and $C_{\text{aliphatic}}$–$C_{\text{aliphatic}}$ bond lengths (1.541–1.552 Å) agree well with those expected for the former (1.528 (B3LYP/DZP)[3] and 1.527 Å (RHF/6-31G)[2]) and for the latter (1.562 (B3LYP/DZP)[3] and 1.557 Å (RHF/6-31G)[2]). The dihedral angle between the C1–C7–C9 and C7–C8–C9 planes is 39.6°, and similar dihedral angles (37.7 and 38.2°) are observed for other bridges. These values are in good agreement with those obtained by MO calculations (38.3° by RHF/6-31G) for the C_{6h} structure.[2] Thus, the most stable C_{6h} structure was observed, for the first time, in the crystals of **1**–TCNQ-F_4. The D_{6h} structure in the crystals of **1** and its TCNQ complex may result from the presence of the **1**(C_{6h}) and **1′**(C_{6h}) conformers (Scheme 1) in a 1:1 ratio in the crystal packing.

In conclusion, we have elucidated the structural parameters of **1** with the C_{6h} symmetry in the **1**–TCNQ-F_4 (1:1) complex. The cyclophane **1** forms 1:1 CT complexes with TCNQ and TCNQ-F_4 with alternating D–A stacking. The observed partial D–A overlap is suitable for the efficient HOMO–LUMO orbital interactions. Our present study may be helpful for the understanding of the CT interactions in the solid state because there have been few reports on the crystal structures of the intermolecular cyclophane CT complexes with TCNQ.[7,8] Our

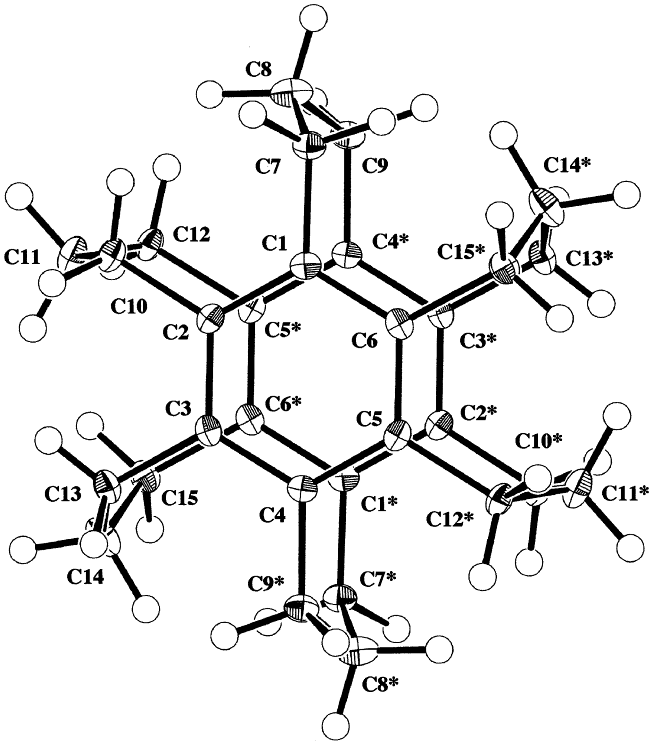


Figure 3. The crystal structure of the cyclophane moiety of **1**–TCNQ-F_4 (1:1) complex at −180°C. Selected bond lengths (Å) and angles (°): C1–C2 1.406(2), C2–C3 1.415(2), C3–C4 1.406(2), C4–C5 1.406(2), C5–C6 1.411(2), C1–C7 1.520(2), C7–C8 1.552(3), C8–C9 1.546(3), C9–C4* 1.523(2), C2–C10 1.520(2), C10–C11 1.549(3), C11–C12 1.541(2), C12–C5* 1.521(2), C3–C13 1.521(2), C13–C14 1.552(3), C14–C15 1.543(3), C15–C6* 1.521(2), C1–C7–C9 and C7–C8–C9 39.6, C2–C10–C12 and C10–C11–C12 37.7, C3–C13–C15 and C13–C14–C15 38.2. Transannular distances: C1–C4* 2.934(2), C2–C5* 2.931(2), C3–C6* 2.929(2)

solid-state structural study of a series of multibridged [3_n]cyclophanes and their hetero analogs, as well as their CT complexes, is now in progress, and the study may lead to the development of new electron-conducting materials.[9]

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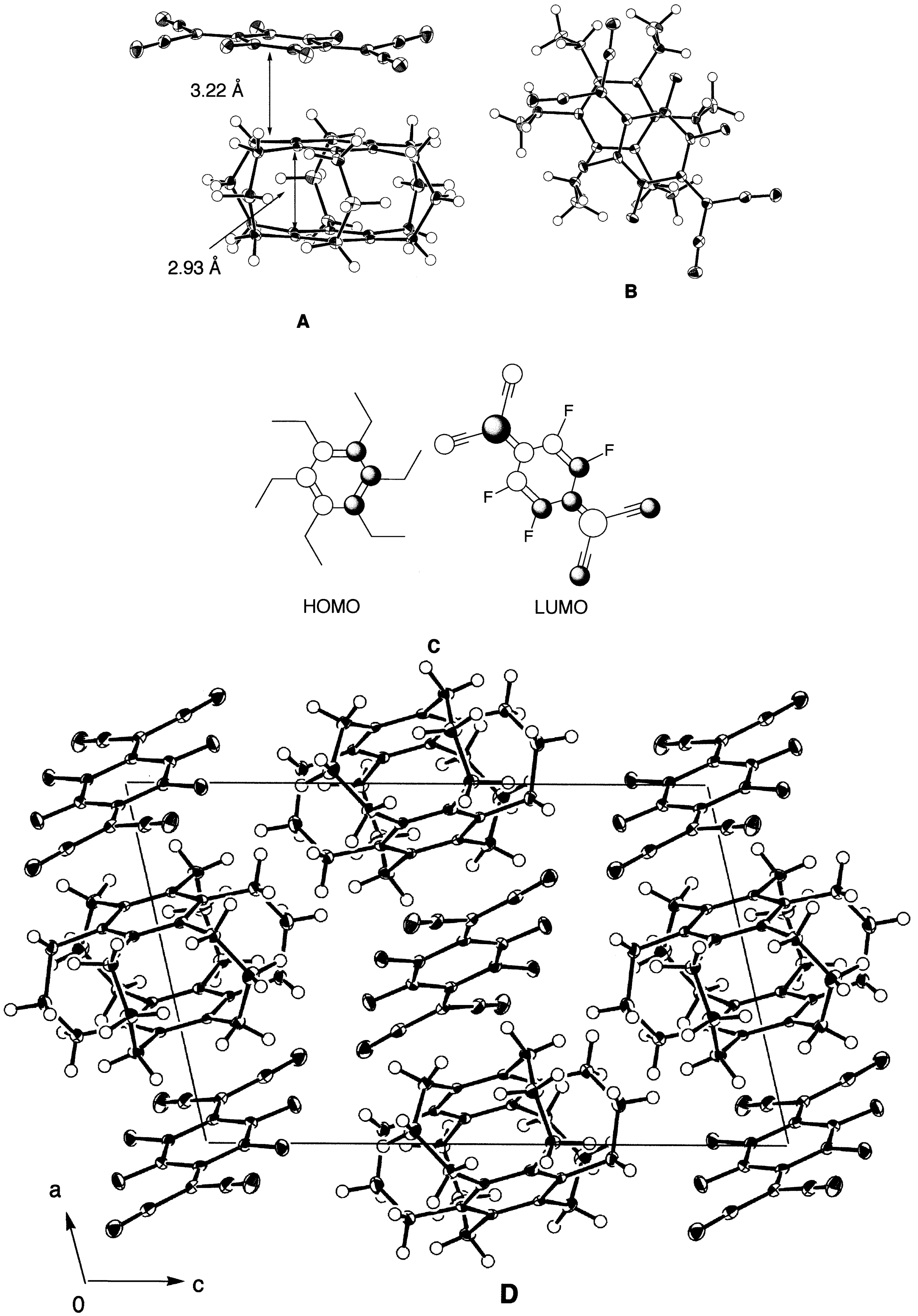

Figure 4. The crystal structure of the **1**–TCNQ-F_4 (1:1) complex at −180°C: side view (A), top view (B), HOMO and LUMO orbitals (C), and crystal packing diagram (D)

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4. Cyclophane **1** was recrystallized from $CHCl_3$, and the crystals of the **1**–TCNQ–benzene (1:1:1) and **1**–TCNQ-F_4 (1:1) complexes were grown by slow evaporation of benzene and CH_2Cl_2, respectively, from an equimolar solution of **1** and an acceptor.

   X-Ray crystal data for **1**–TCNQ ($C_{48}H_{46}N_4$): Rigaku R-AXIS-IV diffractometer, Mo Kα ($\lambda = 0.71070$ Å), crystal dimensions 0.20×0.35×0.25 mm^3 (black prism), $a = 9.583(2)$, $b = 10.444(2)$, $c = 9.551(5)$ Å, $\alpha = 93.20(3)$, $\beta = 115.23(5)$, $\gamma = 91.98(2)°$, triclinic space group $P\bar{1}$ (no. 2), $T = -190°C$, $Z = 1$, $\mu_{Mo} = 0.75$ cm^{-1}, $M_r = 678.92$, $V = 861.5200$ Å^3, anode power 45 kV×250 mA, $\rho_{calc} = 1.308$ g/cm^3, $2\theta_{max} = 55.0°$, $F(000) = 362.00$; of 2283 reflections measured, 1927 were observed ($I > 3.00\sigma(I)$), number of parameters 236. The structure was solved by a direct method and was refined on SCHELEX-86.[10] Data were corrected for Lorentz polarizations. The data/parameter ratio was 8.17. $R = 0.073$, $R_w = 0.121$, GOF = 1.45, max/min residual density +0.43/−0.28 e Å^{-3}.

   X-Ray crystal data for **1** ($C_{30}H_{36}$): Rigaku R-AXIS-IV diffractometer, Mo Kα ($\lambda = 0.71070$ Å), crystal dimensions 0.30×0.25×0.30 mm^3 (colorless prism), orthorhombic, space group *Cmca* (no. 64); $a = 15.471(9)$, $b = 11.435(7)$, $c = 11.325(4)$ Å, $T = -180°C$, $Z = 4$, $V = 2003(3)$ Å^3, $\mu_{Mo} = 0.73$ cm^{-1}, $M_r = 396.61$, anode power 45 kV×250 mA, $\rho_{calc} = 1.315$ g/cm^3, $2\theta_{max} = 55.0°$, $F(000) = 864.00$; of 1115 reflections measured, 814 were observed ($I > 3.00\sigma(I)$), number of parameters 70. The structure was solved by a direct method and was refined on SIR-88.[11] Data were corrected for Lorentz polarizations. The data/parameter ratio was 11.63. $R = 0.087$, $R_w = 0.156$, GOF = 1.72, max/min residual density +0.31/−0.35 e Å^{-3}.

   X-Ray crystal data for **1**–TCNQ-F_4 ($C_{42}H_{36}F_4N_4$): Rigaku R-AXIS-RAPID diffractometer, Mo Kα ($\lambda = 71070$ Å), crystal dimensions 0.10×0.10×0.10 mm^3 (black prism), $a = 10.1825(3)$, $b = 9.4863(2)$, $c = 16.0809(5)$ Å, $\beta = 102.8348(6)°$, monoclinic, space group $P2_1/n$ (no.14), $T = -180°C$, $Z = 2$, $\mu_{Mo} = 1.04$ cm^{-1}, $M_r = 672.77$, $V = 1514.51(7)$ Å^3, anode power 50 kV×40 mA, $\rho_{calc} = 1.475$ g/cm^3, $2\theta_{max} = 55.0°$, $F(000) = 704.00$; of 3439 reflections measured, 2411 were observed ($I > 3.00\sigma(I)$), number of parameters 299. The structure was solved by a direct method and was refined on SIR-92.[12] Data were corrected for Lorentz polarizations. The data/parameter ratio was 8.06. $R = 0.039$, $R_w = 0.052$, GOF = 1.12, max/min residual density +0.38/−0.20 eÅ^{-3}.

   All calculations were performed using the TEXSAN[13] crystallographic software package of the Molecular Structure Corporation. Crystallographic data (excluding the structure factor) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138302 (**1**), no. CCDC-138301 (**1**–TCNQ), and no. CCDC-138300 (**1**–TCNQ-F_4). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-33603; e-mail: deposit@ccdc.cam.ac.uk).
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