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Molecular Structure of Chlorocycloheptane in Inclusion Compound with 9,9′-Biantryl and Gelation during Crystallization

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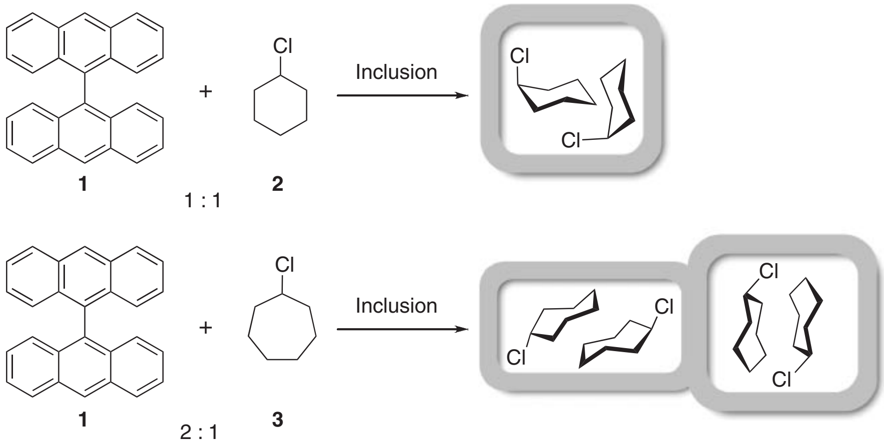
9,9′-Bianthryl formed an inclusion compound with chlorocycloheptane in a 2:1 ratio. X-ray analysis revealed that two guest molecules were accommodated in a cavity surrounded by eight host molecules. The guest molecules were conformationally fixed in each cavity into either of two twist-chair forms that differed in the position of the chloro group. These conformations were compared with the calculated ones for chlorocycloheptane itself by DFT calculation. When the inclusion compound was prepared from a concentrated solution of 9,9′-bianthryl in chlorocycloheptane, the gelation was followed by crystallization. This phenomenon is unusual for relatively small molecules lacking strong intermolecular interactions.

9,9′-Bianthryl (**1**) and related compounds are found to form inclusion compounds with a wide range of small organic molecules.[1–5] In each molecule, the two anthracene planes are nearly perpendicular (dihedral angle 80.5°)[6] and the rotation about the C9–C9′ bond is considerably restricted.[7] These structural features facilitate the formation of cavities for guest molecules upon assembly. X-ray structures of inclusion compounds of 9,9′-bianthryl so far reported reveal that guest molecules are occasionally accommodated in cavities in a less stable conformation to fit the cavity size and shape.[3–5] For example, chlorocyclohexane (**2**) form an inclusion compound with **1** in the axial conformation (Scheme 1),[4] which is less stable than the equatorial conformation,[8] while this guest molecule is included by another host derived from tartaric acid in the equatorial conformation.[9] Conformational analysis of cycloheptane derivatives is more complicated than that of cyclohexane derivatives because of facile interconversions around several possible conformers.[10] Even in the inclusion compound with tris(5-acetyl-3-thienyl)methane, cycloheptane molecules are significantly disordered even at 220 K.[11] Therefore, we employed this unique hydrocarbon host to elucidate the conformation of cycloheptanes in crystal cavities, and used chlorocycloheptane (**3**) as a typical monosubstituted cycloheptane for this purpose. We herein report the X-ray structure of the inclusion compound focusing on the mode of inclusion and the conformation of seven-membered ring moieties. We also found an interesting phenomenon, gelation of a solution of 9,9′-bianthryl in chlorocycloheptane, during the preparation of



Scheme 1. Formation of inclusion compounds of 9,9′-bianthryl with chlorocycloalkanes. Gray bold lines indicate walls constructed by 9,9′-bianthryl molecules.

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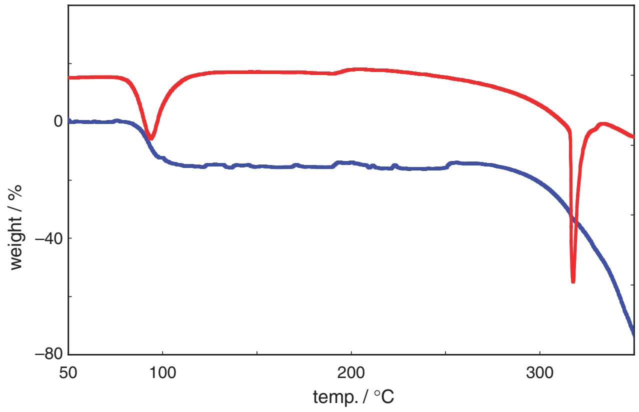

Figure 1. TG (blue, left ordinate)/DTA (red) measurement of 9,9′-bianthryl–chlorocycloheptane (2:1) inclusion compound.

the inclusion compound. The nature and structure of this unique gel consisting of small molecules were examined by microscopic observation and spectroscopic measurements.

Results and Discussion

Preparation and Characterization of Inclusion Compound. An inclusion compound was prepared by crystallization from a solution of 9,9′-bianthryl (20 mg) in chlorocycloheptane (0.50 mL) to give pale yellow prisms in 72% yield. The host–guest ratio of the inclusion compound was determined from the signal intensities of the ^{1}H NMR spectrum to be 2:1, and this composition was consistent with microanalysis and X-ray analysis. Guest molecules slowly escaped from the crystals of the inclusion compound upon standing under ambient conditions with loss of their transparency. Thermal measurements revealed that guest molecules were endothermically released from the crystals at 94 °C (cf. chlorocycloheptane, bp 175 °C) with 15% decrease of weight (calcd 16%) and the remaining guest-free material melted at 317 °C with partial sublimation at >280 °C (Figure 1). The guest-free 9,9′-bianthryl melted at 317 °C, consistent with literature data.[6a]

The IR spectrum of the inclusion compound in the solid state is practically an overlap of that of **1** in the solid state and that of neat chlorocycloheptane. This observation suggests the absence of strong interactions between host and guest molecules. The C–Cl stretching vibration bands of chlorocycloheptane appeared at 710, 680, and 636 cm^{-1}.[12] However, as these bands overlapped with the strong bands assigned to the host (785 and 730 cm^{-1}) for the inclusion compound, they provide little information on the conformational changes of the guest molecules.

Crystallization via Gelation. When we tried to prepare the inclusion compound from a concentrated solution, the solution became cloudy before forming crystals. This substance was highly viscous and scattered light, evidence of gel formation. When a solution of host (20 mg) in chlorocycloheptane (0.30 mL) was allowed to stand at 20 °C, gelation was initiated after 4–5 min and was completed after 9–10 min (Figure 2). Then, crystallization began after 30–40 min and the gel structure slowly disintegrated with the growth of crystals. Finally, the gel completely disappeared after 3.5 days to give a mixture of inclusion crystals and a supernatant solution. Although the course of gel formation and crystallization was somewhat influenced by experimental conditions, the gel state was maintained at least for a few days in all cases. This gel forms a fiberous structure as shown in the micrograph in Figure 3.[13] The fibers extend to the nearly same direction, and their diameter is estimated to be ca. 2–5 µm. The XDR profile of this material showed a very broad halo peak, which disappeared with the appearance of new peaks as the gel structure was broken. This finding means that molecules are assembled in the gel state with low crystalline nature.

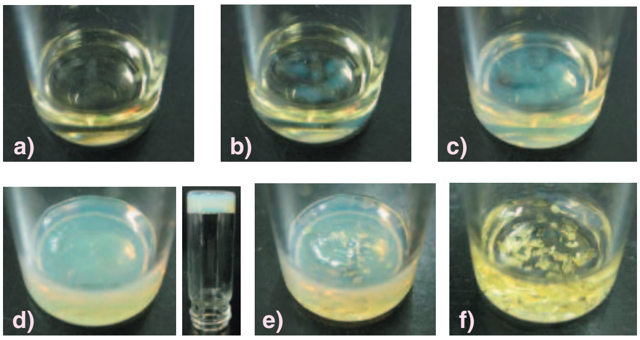

Figure 2. Course of gel formation and crystallization of a solution of 9,9′-bianthryl in chlorocycloheptane. Times after dissolution: a) 0 min, b) 5 min, c) 7 min, d) 9 min, e) 20 h, and f) 85 h.

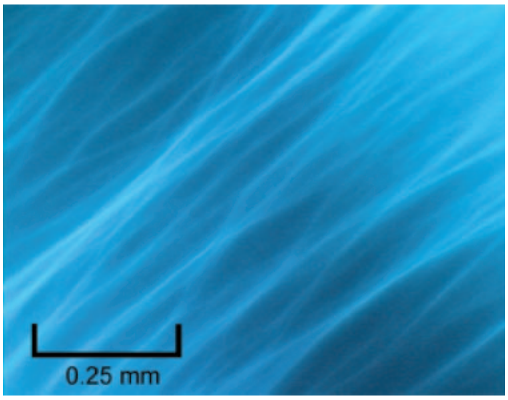

Figure 3. Polarizing optical micrograph of gel formed in a solution of 9,9′-bianthryl in chlorocycloheptane.

This phenomenon was also observed for other haloalkanes and hydrocarbons, such as *trans*-1,2-dichlorocyclohexane, isopropylcyclohexane, and *p*-xylene. To our knowledge, gel formation is rarely found in relatively small molecules lacking both of long alkyl chains and strong intermolecular interactions involving the hydrogen bond.[14,15] Hence, 9,9′-bianthryl is a unique hydrocarbon as a low molecular mass gelator. This phenomenon suggests that host molecules construct a polymeric network as a metastable state, where intermolecular $\pi\cdots\pi$ or CH$\cdots\pi$ interactions play important roles. The scope and limitation of the gel formation and its details will be reported elsewhere.

X-ray Analysis. The X-ray structure of the inclusion compound is shown in Figure 4. An asymmetric unit contains four host and two guest molecules, and there are neither significant disorders nor thermal displacements in all non-hydrogen atoms. In each host molecule, the two 9-anthryl groups are nearly perpendicular as revealed by the dihedral angles of −83, −85, +79, and +78° for independent molecules. These values are comparable to those of other 9,9′-bianthryl compounds: guest-free compound (80°),[6a] α-ionone clathrate (88°),[2] chlorocyclohexane clathrate (84 and 89°),[4] and benzene clathrate (86°).[3]

The two chlorocycloheptane molecules take different conformations as shown in Figure 5 together with the torsion angles within the ring carbon chains. Torsion angle notations for molecules A and B are $+-+-+-+$ and $-+-+-+-$ (starting from C1), respectively, corresponding to twist-boat conformations.[16,17] The ring structure is approximately C_2 symmetric with a C_2 axis passing through the C1 atom and the middle point of C4–C5 bond. A chlorine atom is attached to C1 in molecule B, whereas it is attached to C4 at pseudoequatorial position (C4-e) in molecule A. Cycloheptane and its derivatives are conformationally fluxional in the liquid state or in solution: interconversion between several twist-chair and other conformations takes place rapidly via pseudorotation.[8,10,17] DFT calculations were carried out for various conformers of chlorocycloheptane at B3LYP/6-31G(d) level. We found four kinds of twist-chair conformations as energy-minimum structures within the range of 2.5 kJ mol^{-1}, where the chlorine atom was attached to C1, C2-e, C3-e, or C4-e atom (Figure 6). The inclusion compound formation with 9,9′-bianthryl freezes the conformation of chlorocycloheptane into the C1 and C4-e forms. It should be noted that two different conformers are observed in a single inclusion compound.

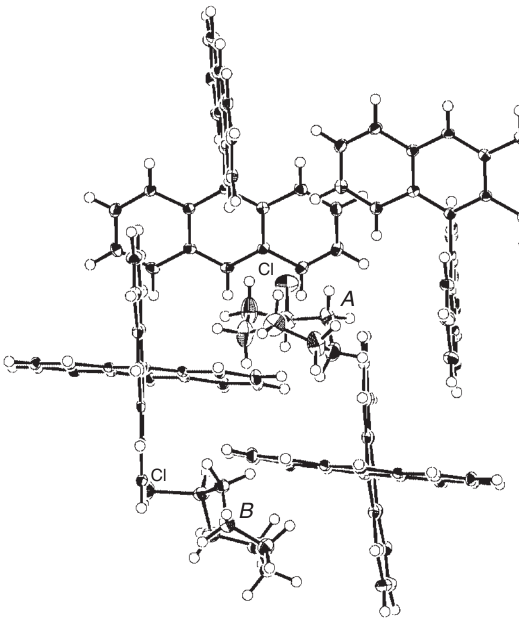

Figure 4. ORTEP drawing of 9,9′-bianthryl–chlorocycloheptane (2:1) inclusion compound with thermal ellipsoids at 50% probability.

Packing diagrams are shown in Figure 7, where guest molecules are drawn as a space filling model. Two guest molecules are included in each cavity surrounded by eight host molecules. This inclusion mode is similar to that of inclusion compounds with benzene, α-ionone, and chlorocyclohexane.[2–4] Two types of cavities are aligned alternately along columns extending in three directions. In cavity X, molecule A and its enantiomeric form are accommodated in face-to-face orientation to form a cubic-like cage. In the next cavity Y, molecule B and its enantiomeric form are accommodated in a nearly flanking orientation to form a long hexahedral cavity. In each pair of guest molecules, chlorine atoms point toward opposite directions. The host network is constructed mainly with C–H···π interactions rather than π···π interactions, as revealed by several C–H···π contacts at ca. 2.80 Å. There are no significant contacts (C–H···π and C–H···Cl) between host and guest molecules and between guest molecules. These data indicate that size and shape selectivity plays an important role in the clathrate formation of 9,9′-bianthryl. It is interesting that this host constructs two types of cavities for only one guest compound, thereby effectively differentiating the conformation of guest molecules.

Experimental

General. 9,9′-Bianthryl was prepared according to the method reported in the literature.[18] Chlorocycloheptane was purchased form TCI. Melting points are uncorrected. ^{1}H NMR spectra were measured on a JEOL Lambda-300 at 300 MHz. IR spectra were measured on a JASCO FT/IR-460 spectrometer with a DuraScope attachment by the ATR method. Elemental analyses were performed with a Perkin-Elmer 2400 series analyzer.

Preparation of Inclusion Compound. 9,9′-Bianthryl (20 mg, 0.056 mmol) was dissolved in chlorocycloheptane (0.50 mL) by heating at 160 °C for 3 min. The solution was allowed to stand at room temperature for 7 days and the formed crystals were collected. Pale yellow prisms; yield 17 mg (72%); mp 314.0–314.5 °C; IR (ATR) 3047, 2922, 2853, 1440, 1315, 1012, 885, 857,

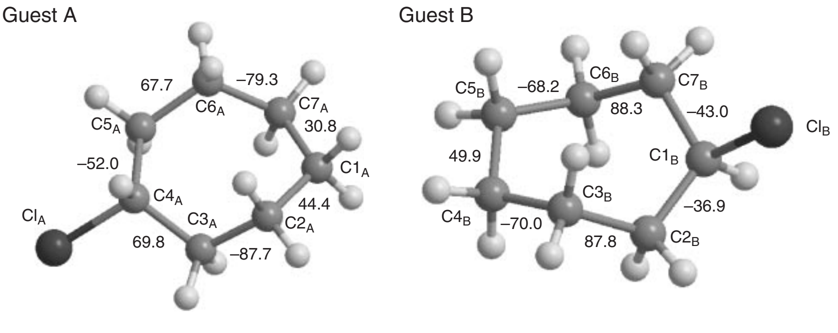

Figure 5. X-ray structures of chlorocycloheptane molecules in the inclusion compound. Torsion angles along ring carbon chains are given at the central C–C bonds. For example, the torsion angle of C1–C2–C3–C4 is indicated at the C2–C3 bond.

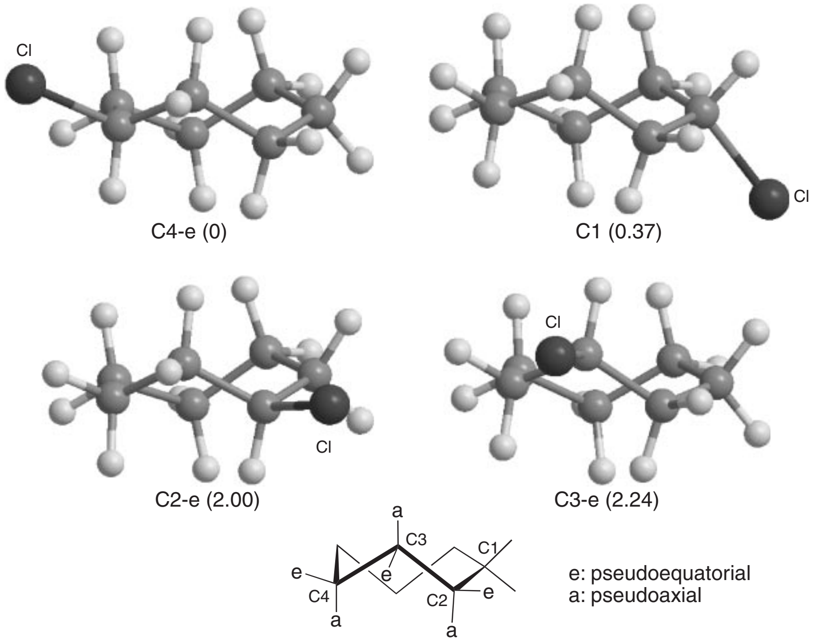

Figure 6. Conformers of chlorocycloheptane optimized by B3LYP/6-31G(d) method. Relative energies (kJ mol^{-1}) are indicated in parentheses.

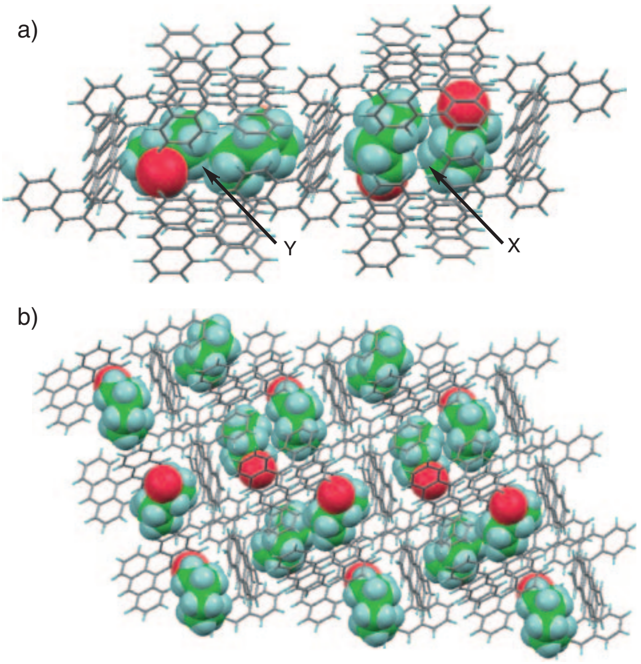

Figure 7. Packing diagram of 9,9′-bianthryl–chlorocycloheptane (2:1) inclusion compound. Guest molecules are represented as space filling model (Cl: red, C: green, H: light blue). a) Four guest molecules in two cavities and surrounding host molecules. b) Extended cavity network.

835, 783, 726, 668, 640, 598 cm^{-1}; Anal. Found: C, 89.61; H, 6.07%. Calcd for $2(C_{28}H_{18})\cdot(C_7H_{13}Cl)$: C, 89.92; H, 5.87%; ^{1}H NMR ($CDCl_3$): δ 1.46 (2H, m), 1.50–1.61 (4H, m), 1.73 (2H, m), 1.90 (2H, m), 2.15 (2H, m), 4.17 (1H, m), 7.05–7.18 (16H, m), 7.44 (8H, t, $J = 8.6$ Hz), 8.15 (8H, d, $J = 8.6$ Hz), 8.68 (4H, s). Aliphatic and aromatic signals are consistent with those of chlorocycloheptane and 9,9′-bianthryl.

Gelation Experiments. 9,9′-Bianthryl (20 mg, 0.056 mmol) was dissolved in chlorocycloheptane (0.30 mL) by heating at 160 °C for 3 min. The solution was allowed to stand at room temperature, and its state was visually observed at appropriate intervals. Crystals formed via gelation were identical with the crystals prepared as above. Micrographs were observed on an Olympus BX50 microscope through a polarizing filter (open nicol) with a magnification of 300× (eyepiece 15×, objectives 20×). XRD data were collected on a Rigaku RINT2000 diffractometer with Cu Kα radiation ($\lambda = 0.15418$ Å). A sample was mounted on a glass plate.

Thermal Analysis. Thermal data were acquired with a Shimadzu simultaneous TG/DTA instrument DTG-60/60H. The temperature was raised at a rate of 10 °C min^{-1} with ca. 2 mg of a sample of the inclusion compound or the guest-free host.

DFT Calculation. Conformational search of chlorocycloheptane was carried out on CONFLEX ver. 5 program[19] with MMFF94s force field to give 10 independent structures. Each structure was further optimized at the B3LYP/6-31G(d) level with Gaussian 03 program.[20]

X-ray Analysis. A single crystal of the inclusion compound was prepared as described above and its dimensions were $0.10 \times 0.10 \times 0.06$ mm^3. Diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° at −150 °C. Reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method (SHELXS97)[21] and refined by the full-matrix least-squares method (SHELXL97).[22] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions. Formula $C_{126}H_{98}Cl_2$, $M_r = 841.47$, triclinic, space group $P\bar{1}$ (#2), $a = 15.5757(3)$, $b = 17.6166(2)$, $c = 18.9120(3)$ Å, $\alpha = 107.1795(10)$, $\beta = 113.8779(19)$, $\gamma = 93.6436(12)$°, $V = 4432.72(12)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.26$ g cm^{-3}, μ(Mo Kα) = 1.29 cm^{-1}, number of data 17415, number of data used 13628 ($I > 2.0\sigma(I)$), $R1 = 0.0533$, $wR2 = 0.1356$, GOF = 1.029. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC 703850. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

IR spectra of 9,9′-bianthryl, chlorocycloheptane, and the inclusion compound (Figure S1) and XRD charts of the gel and the inclusion compound (Figure S2). These materials are available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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