SELECTION OF GUEST INCLUSION GEOMETRY BY A SERIES OF WATER-SOLUBLE PARACYCLOPHANES HAVING WELL-DEFINED HYDROPHOBIC CAVITIES

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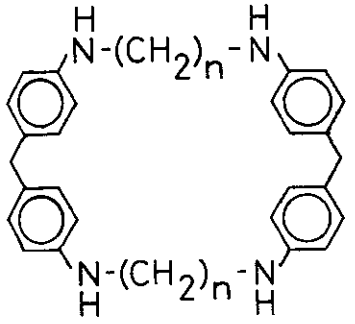
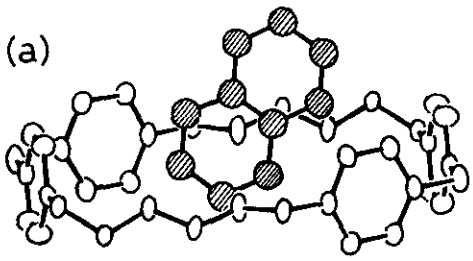
Our crystallographic[1] and NMR spectral[2] studies have shown that a novel, diphenylmethane-containing paracyclophane CP44, soluble in acidic water (pH < 2), forms inclusion complexes with hydrophobic guests, and that the guest inclusion occurs in a particular geometry and not in a random manner. Here we report our recent findings that the inclusion geometry of the guests is markedly sensitive to slight structural changes of the hydrophobic cavities of the hosts.

A series of paracyclophanes (CPnn, n = 4 - 8) were synthesized, and the inclusion geometries of their complexes with several hydrophobic guests (e.g., naphthalene, durene) were investigated by X-ray crystallography and ^{1}H NMR spectroscopy. Comparison of the crystal structures of the complexes formed with naphthalene by the protonated CP44 (Fig. 1a) and CP55 (Fig. 1b) evidently shows a dramatic change of the guest inclusion geometry despite the difference of only one methylene unit in these hosts. A similar change of the guest inclusion geometry was also observed in solution (DCl-D_2O/CD_3OD = 1:1) by ^{1}H NMR experiments.

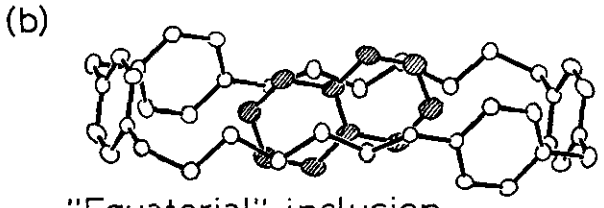
Thus, control of guest inclusion geometry was successfully effected by this simple system, affording an important basis for the control of organic reactions by host-guest complex formation.



CPnn
CP44 (n = 4)
CP55 (n = 5)



"Pseudoaxial" inclusion



"Equatorial" inclusion

Figure 1 Crystal structures of (a) CP44·4H$^+$-naphthalene complex and (b) CP55·4H$^+$-naphthalene complex.

1) K. Odashima, A. Itai, Y. Iitaka, and K. Koga, J. Am. Chem. Soc., 102, 2504 (1980).
2) K. Odashima, A. Itai, Y. Iitaka, Y. Arata, and K. Koga, Tetrahedron Lett., 21, 4347 (1980).