

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

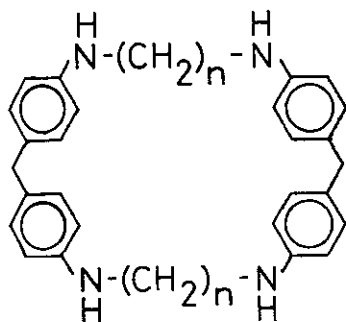
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Our crystallographic¹ and NMR spectral² studies have shown that a novel, diphenylmethane-containing paracyclophane CP44, soluble in acidic water (pH < 2), forms inclusion complexes with hydrophobic guests, and that the guest inclusion occurs in a particular 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 (CP_n, 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 ¹H 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-D₂O/CD₃OD = 1:1) by ¹H NMR experiments.

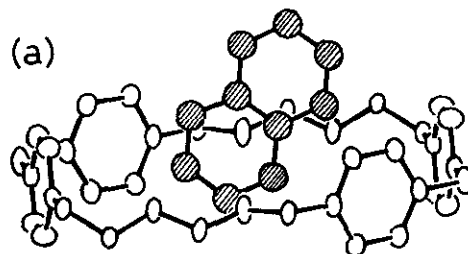
Thus, control of guest inclusion geometry was successfully effected by this simple system, affording an important basis for the control of organic reactions by host-guest complex formation.



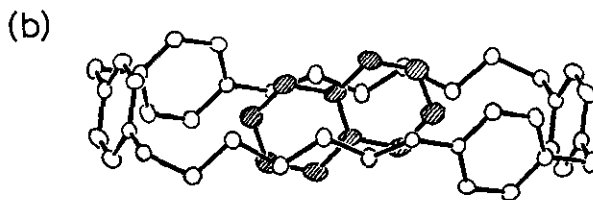
CP_n

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).