

Exploring the Relationship between Complex Conformation and Chiral Discrimination and Induction in Cyclodextrin Systems

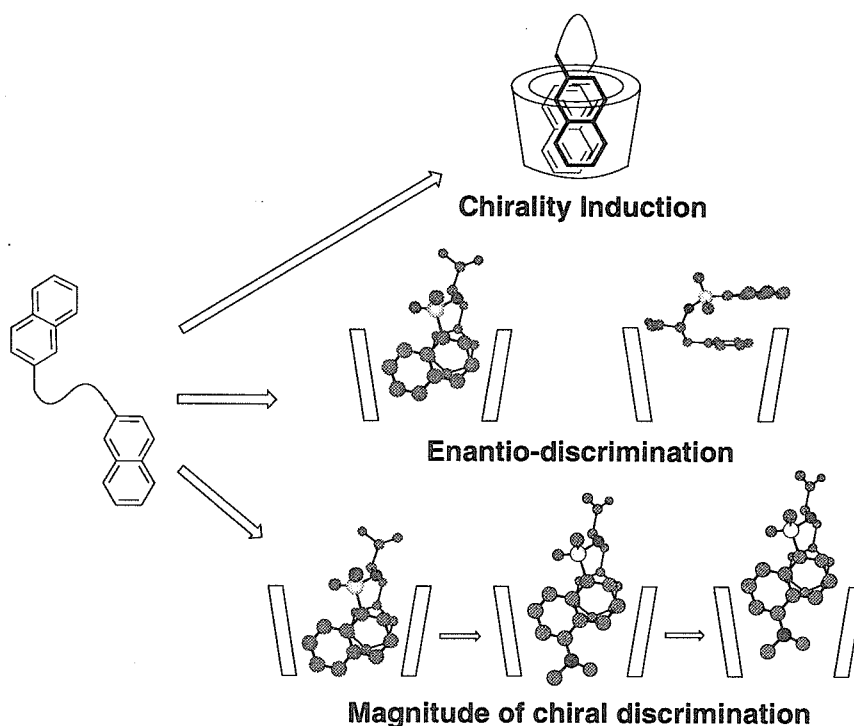
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シクロデキストリン系における包接錯体の構造と
不斉識別および不斉誘導

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Natural and modified cyclodextrins (CDs) have received much attention over recent years as aqueous based hosts for studying the chiral molecular recognition process of organic molecules. However, the underlying mechanism(s) of chirality induction and the discrimination between enantiomers remains poorly understood. To contribute to the elucidation of the nature of these phenomena in natural CDs we have studied both chirality induction and discrimination events in both chiral and achiral naphthalene derivatives. Detailed analysis of the complexation characteristics of naph-D/L-phe and dans-D/L phe with β - and γ -CDs highlight that even small structural variations in either host or guest can lead to significant changes in the resulting complex s structure, and consequently the observed chiral discrimination. A correlation was found between the relative orientations of the host s and guest s chiral groups and the observed chiral discrimination. Further, and for the first time, direct evidence was obtained correlating the host-guest complex conformation with the magnitude of chiral discrimination, and not just for the enantiomeric preference (D or L). Thus leading to greater understanding of the mechanisms behind chiral discrimination.



For certain achiral bis-naphthalenes the adoption of an intra-molecularly stacked form can result in a number of planar type chiral conformations. The hydrophobic chiral cavities of β - and γ -CDs were utilised to promote such intramolecular stacking and to discriminate between the induced enantiomers of the planar chiral species. For an ester tethered species it was possible to promote increased intramolecular stacking and complexation by the 'counterintuitive' addition of ethylene glycol, via two O-H...O hydrogen bonds between the ethylene glycol and tether, acting as a molecular clip to 'lock' the two naphthalenes in a stacked conformation. This has the effect of enhancing the chirality induction through pre-organisation and a corresponding reduction in entropy loss on complexation.