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Induced-fit adjustability of flexible molecular clefts composed of convergent quinolyl groups: a sizable selectivity arising from structural complementarity of aromatic guest and aromatic spacer of the host

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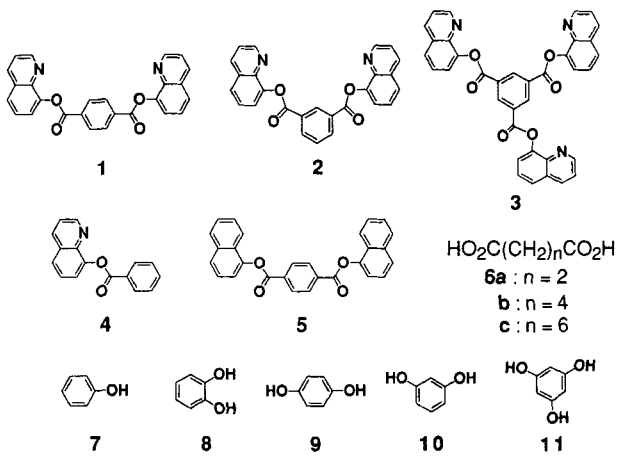
8-Quinolyl esters of benzenepolycarboxylic acids form flexible molecular clefts composed of convergent quinolyl groups. 1,4-Disubstituted diquinolyl terephthalate, but not monosubstituted quinolyl benzoate, in $CDCl_3$ extracts succinic acid and forms a two-point hydrogen-bonded complex with 1,4-dihydroxybenzene. 1,3,5-Trisubstituted triquinolyl trimesate in $CDCL_3$-DMSO-d_6 (97/3) forms one-point, two-point, and three-point hydrogen-bonded adducts with phenol ($K \cong 1$ and $-\Delta G^0 \cong 0$), 1,3-dihydroxybenzene ($K = 24$ and $-\Delta G^0 = 2.2$), and 1,3,5-trihydroxybenzene ($K = 120\,M^{-1}$ and $-\Delta G^0 = 3.3$ kcal/mol at 298 K), respectively. 1,3-Disubstituted diquinolyl isophthalate forms two-point adducts of similar stability with both 1,3-dihydroxy- ($K = 12$) and 1,3,5-trihydroxybenzene ($K = 13$). These results suggests that the present molecular-clefts having otherwise flexible ester linkages readily undergo induced-fit adjustment to multifunctional guest structures and the selectivity arises from the structural complementarity of aromatic guest and aromatic spacer of the host.

Selectivity is an important aspect of molecular recognition. The selectivity exhibited by *rigid* molecular clefts has been well documented.[1-4] *Flexible* clefts, on the other hand, have been receiving much less attention. Along these lines, we prepared flexible molecular clefts composed of convergent quinolyl groups. We report here that they show a sizable selectivity in the induced-fit accommodation of dicarboxylic acids and polyhydroxybenzenes as guests.[5]

Reaction of 8-quinolinol with terephthaloyl, isophthaloyl, or trimesoyl chloride in ether-triethylamine containing 4-dimethylaminopyridine afforded 1,4-di-, 1,3-di-, and 1,3,5-triquinolyl esters **1** (54%), **2** (56%), and **3** (43%), respectively.[6] Monoquinolyl and dinaphthl references **4** and **5** were obtained similarly.[6] Solid-liquid extraction of otherwise chloroform-insoluble dicarboxylic acids, $HO_2C(CH_2)_nCO_2H$ (**6**), was carried out by stirring well-pulverized **6** (0.1 mmol) with a $CDCl_3$ solution (1.0 ml) of host **1** or reference host (5.0 mM) for 24 h at 298 K. The extractabilities of **6**, as expressed by ^{1}H-NMR determined **6**/host molar ratio in the organic phase, are 0.32 (**6c**), 0.17 (**6b**), 0.12 (**6c**) when host = **1** and ~0 (**6a**), 0.10 (**6b**), 0.20 (**6c**) when host = **4**. Dinaphthyl reference **5** was



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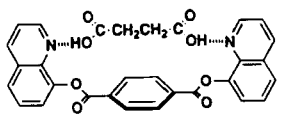
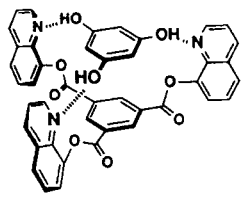
unable to extract any quest. It is interesting to note the reverse selectivities of hosts **1** and **4** with respect to the methylene chain-lengths (n) in the guests. Thus, succinic acid (**6a**) shows a very high selectivity for **1** over **4**, while the selectivity is even reversed for suberic acid (**6c**). These results, coupled with examination of molecular models, indicate that the **1-6** complexation involves a chain-length dependent two-point hydrogen-bonding,[5,7] as illustrated for complex **1-6a**.[8] On the other hand, the lipophilicity of **6** is the major governing factor in the one-point **4-6** complexation.



1·6a



3·11

Hosts **1** and **4** also form 1:1 (confirmed by Job plots)[9] complexes with phenol (**7**), catechol (**8**), and hydroquinone (**9**) in $CDCl_3$, as readily monitored by the complexation-induced ^1H NMR downfield shift of the guest OH-proton resonance or upfield shifts of the terephthaloyl or benzoyl ring-protons of the host. The binding constants (K) evaluated by the Lang's modification[10] of the Benesi-Hildebrand analysis of the titration data are summarized in Table 1. Monofunctional guest phenol (**7**) is weakly bound to hosts **1** and **4** with similar K's. Ortho-dihydroxy compound **8** is somewhat more strongly bound without any notable selectivity again. The para isomer **9**, however, is much more discriminate. It binds to the two-point host **1** one-order of magnitude more firmly than to the one-point host **4**.[11]

The complexation of practically chloroform-insoluble resorcinol (**10**) and phloroglucinol (**11**) as well as phenol (**7**) with hosts **2**, **3**, and **4** was investigated for solutions in $CDCl_3$-DMSO-d_6 (97/3 v/v) in a similar manner as above. The binding constants are summarized in Table 2. One-point host **4** or guest **7** shows only a very low affinity to any guest or host. 1,3-Disubstituted two-point host **2** or guest **10** allows larger K's for two-point or three-point guests or hosts. 1,3,5-Trisubstituted three-point host **3** or guest **11**, on the other hand, exhibits a steady and remarkable increase in binding ability on goind from one-point through two-point to three-point guests (**7** < **10** < **11**) or hosts (**4** < **2** < **3**). These results clearly indicate that the present hosts are capable of induced-fit adjustment to the multifunctional guest structures, allowing one-point ($K \cong 1$, $-\Delta G^0 \cong 0$), two-point ($K \cong 10$, $-\Delta G^0 \cong 1.6$), or three-point ($K \cong 100\,M^{-1}$, $-\Delta G^0 \cong 3.2$ kcal/mol at 298 K) host-guest hydrogen-bonding, as illustrated for complex **3-11**.[11,12]

The present *flexible* molecular clefts **1-3** show, as expected, rather poor guest-binding abilities, as compared with those of recently-reported *rigid* polyhydroxybenzene-receptors such as a cage-like host having three convergent bipyridine moieties ($K = 11\,000\,M^{-1}$ for guest **11** in CD_2Cl_2)[3] and a molecular clip (K up to $5400\,M^{-1}$ for guest **9** in $CDCl_3$).[4] Nevertheless, they show sizable selectivities in the induced-fit accommodation of the guests. The selectivity essentially and simply arises from the structural complementarity, in terms of substitution pattern, of aromatic guest and aromatic spacer of the host; there is a good correlation between the number of binding contacts and the complex stability. The present approach provides a synthetically very simple general strategy for the design of receptors for particular (hetero)aromatic guests.

Table 1 Binding constants of hosts **1** and **4** with guests **7**, **8** and **9** in $CDCl_3$ at 298 K

		guest		
host		**7**	**8**	**9**
$K(M^{-1})$	**1**	4.9	21	100
	4	5.3	24	8.2

Table 2 Binding constants of hosts **2**, **3** and **4** with guests **7**, **10** and **11** in $CDCl_3$-DMSO-d_6 (97:3 v/v) at 298 K[a]

		guest		
host		**7**	**10**	**11**
$K(M^{-1})$	**2**	~1	12	13
	3	~1	24	120
	4	~1	~1	~1

[a] The binding constants $K \cong 1$ are only approximate since, under these high-concentration conditions, the host-guest complexation is in competition with host-host, guest-guest, host-DMSO, and/or guest-DMSO interactions.

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6 All the host compounds were fully characterized: mp's 111–113, 190–192, 254–255, 234–236, and 217–218°C for compounds **1**, **2**, **3**, **4**, and **5**, respectively.
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8 The ^{1}H NMR($CDCl_3$) and IR($CHCl_3$) spectra for bound **6a** show a single and complexation-induced *upfield-shifted* (by 0.34 ppm) resonance for the methylene protons and a single $\nu_{C=O}$ at 1710 cm^{-1}, respectively. These results indicate that bound **6a** is located above the benzene ring of host **1**. Molecular mechanic calculation using the Nemesis program supports the suggested structure with calculated O—H···N distance and angle of 2.94 Å and 160°, respectively.
9 The 1:1 stoichiometry even for the **1-7** complexation may indicate that π-π stacking makes an important contribution to the binding of host **1** and guest **7**.
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11 Titration for the **1-9** and **3-11** complexation was carried out by monitoring δ_{OH} for the guest ([**9**] = 2.75 mM and [**11**] = 2.60 mM): δ_{OH} = 4.41 and 6.28 for **9** respectively at [**1**] = 0 and 6.77 mM in $CDCl_3$ and δ_{OH} = 7.87 and 8.52 for **11** respectively at [**3**] = 0 and 10.0 mM in $CDCl_3$-DMSO-d_6. The calculated δ_{OH} at saturation binding are 9.45 for **9** and 8.88 for **11**.
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