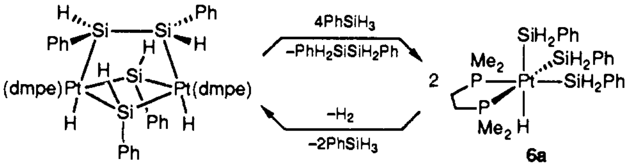
termined (Figure 2). Complex **6a** thermally decomposes at 60 °C with loss of H_2 and $PhSiH_3$ (but not PhH_2SiSiH_2Ph) to regenerate **5a** (eq 2).



5a **6a** (2)

These results emphasize the potential importance of Pt(IV) intermediates in catalytic reactions of hydrosilanes. It is perhaps significant that in the reactions above stoichiometric Si–Si bond formation is observed only upon production of bimetallic complexes **1a–c** or the "basket" molecules **5a,b**, which represent a new structure resulting from Pt-mediated dehydrocouplings. The observed interconversion of **5a** and **6a** (eq 2) suggests that dehydrocoupling mechanisms might be more complicated than those originally considered and lends further credence to the notion that Si–Si bond formation may require two platinum centers acting cooperatively.[1d,3c] The cycle of eq 2 may in fact be catalytic, since both **5a** and **6a** act as a catalysts for the slow dehydrocoupling of $PhSiH_3$ to PhH_2SiSiH_2Ph.[9]

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Supplementary Material Available: Experimental procedures and characterization data for **1–6** and tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **5a**·OEt_2 and **6a** (24 pages); listings of observed and calculated structure factors for **5a**·OEt_2 and **6a** (31 pages). Ordering information is given on any current masthead page.

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(9) For example, thermolysis of **6a** at 95 °C with an 80-fold excess of $PhSiH_3$ produced 4.5 equiv PhH_2SiSiH_2Ph/**6a** after 2 weeks. Of course, the complexes in eq 2 may be merely "resting states" for true catalytic intermediates. For example, it seems possible that **6a** might serve as a precursor to (dmpe)Pt$(SiH_2Ph)_2$, which actually participates in the catalytic cycle.

Remarkable Shape Selectivity in the Molecular Recognition of Carboxylate Anions in Aqueous Solution

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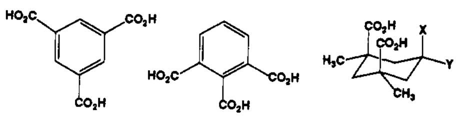
Molecular recognition of polycarboxylic acids and their anions has received much attention in the last few years.[1-6] Size and shape specificity or chain length selectivity in the binding of dicarboxylic acids has been attained in nonpolar solvents by using preorganized receptors.[4,5] In protic solvents, the situation becomes, however, more complex as solvation can compete with host–guest interactions. Highly charged polyammonium macrocycles have been studied as receptors for carboxylate anions in water,[1,2,6] and moderate chain length selectivities have been described. Mainly, structurally very simple anions derived from linear α,ω-dicarboxylic acids were used in these studies. However, it is generally assumed that preorganization plays an essential role in host–guest chemistry.[7] In order to gain further insight into the factors governing anion coordination chemistry, we have studied the interaction of polyammonium receptors and a series of "preorganized" polycarboxylate anions. Here we report on the interactions between the macrocyclic receptor 1,4,7,10,13,16,19-heptaazacyclohenicosane ([21]aneN_7)[8] and the tricarboxylic acids **1–5**, illustrating how small structural modifications in the rigid substrates greatly affect their interaction.

Scheme I



1 2

3 : X = CO_2H, Y = CH_3
4 : X = CH_3, Y = CO_2H

Table I. Logarithm of the Stepwise Basicity[a] and Stability[b] Constants (log *K* (±0.1)) for the Interaction between [21]andN_7 and Tricarboxylate Anions Determined at 298.15 K in 0.15 mol dm^{-3} $NaClO_4$ in Aqueous Solution

	A				
reaction	**1**	**2**	**3**	**4**	**5**
A + H	4.4	5.4	7.3	6.9	5.4
AH + H	3.7	3.9	6.2	4.7	4.2
AH_2 + H	3.0	2.7	3.6	3.8	2.7
A + H_3L	3.1	3.2	3.4	2.5	
A + H_4L	4.6	5.2	5.2	4.0	2.7
A + H_5L	6.2	8.2	8.6	6.6	4.6
A + H_6L	8.0	11.0	12.9	9.7	6.6
A + H_7L	10.0	12.7	15.7	11.7	8.1

[a] As defined by the equation: $AH_n + H \rightleftarrows AH_{n+1}$. [b] As defined by the equation: $A + LH_n \rightleftarrows ALH_n$. In both equations, charges have been omitted for clarity.

Carboxylates derived from benzenetricarboxylic acids (**1** and **2**) can be considered as ideal models for rigid anionic substrates having well defined shapes in terms of both charge density and hydrogen bonding. Kemp's triacid **3**[9] and its cis,trans isomer **4**[10]

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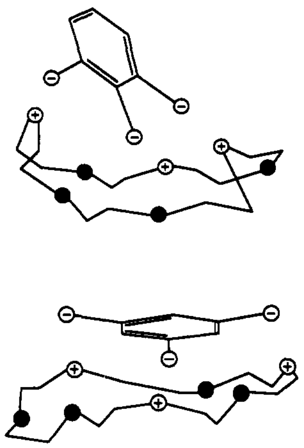
Scheme II



also display relatively rigid structures because of their simple conformational equilibria. Both **3** and **4** and their mono- and dianions adopt the chair conformations with the three or two *cis*-carboxyl groups axial. For the trianions, the conformer with the three or two *cis*-carboxylate groups equatorial is found to be the most stable[11] (Scheme I).

The basicity constants for the tricarboxylates and the stability constants for the complexes formed have been determined in aqueous solution by potentiometry at 298.15 K in 0.15 mol dm^{-3} NaClO$_4$.[12] The stepwise stability constants relative to the interaction of [21]aneN$_7$ with the tricarboxylate anions (A), as well as the basicity constants, are presented in Table I.

The first aspect to be noticed is that substrates **1–4** interact with [21]aneN$_7$ much stronger than the more flexible citrate anions used as a reference. A straight comparison between citrate and 1,2,3-benzenetricarboxylate anions can be made since their basicities are comparable. All of the stepwise stability constants for substrate **2** are about 3 orders of magnitude greater than those for citric acid (**5**). This figure represents one of the highest selectivities reported up to now ($K(\mathbf{2})/K(\mathbf{5}) > 1000$) in the interaction of polycarboxylate anions with polyammonium receptors in aqueous solution.[1,2,6] A direct comparison between **1**, **3**, **4**, and **5** could be difficult because of the different basicities involved, but distribution diagrams calculated from the constants revealed a situation very similar to that found in the former case, the percentage of bound substrate being much higher for **1–4** than for **5** at any pH value.

When comparing both aromatic acids (**1** and **2**), some points can be highlighted. The equivalence of the stepwise stability constants for the complexes H$_3$LA in both acids is remarkable. These species represent the interaction of the tricarboxylate with the triprotonated macrocycle. If electrostatic factors were the only ones controlling the interaction, the stability constants associated with the tricarboxylate of **2** would always be much higher than those for the trianion of **1**. In order to explain this situation, molecular modeling studies have been undertaken. Preliminary results[13] suggest a very good structural complementarity of the tricarboxylate of **1** and triprotonated [21]aneN$_7$. But in the case of the trianion of **2**, an appropriate interaction would require a partial unfavorable folding of the receptor. Thus, it seems that the better structural factor of **1** compensates the higher charge density of **2**. For more protonated complexes, a moderate selectivity of **2** over **1** is always observed (Scheme II).

Finally, the case of the two isomers **3** and **4** can be considered. Some selectivity is observed even for the interaction of the tricarboxylates with the triprotonated ligand ($K(\mathbf{3})/K(\mathbf{4}) = 8$). In the cis,cis isomer, the three carboxyls on the same side of the cyclohexane ring are better disposed for hydrogen bonding. Selectivity is maintained throughout the pH range, and distribution diagrams show how, for the same conditions, the percentages of complexed species are much greater in the case of the cis,cis isomer.

Further work is in progress to study in more detail the structural aspects of those interactions. However, the present results clearly show how preorganization of the substrate in a shape that could be complementary to that of the receptor can be of major importance in host–guest chemistry, giving rise to very high selectivities even in aqueous solution, and how minor structural changes, when producing complementarity differences, do affect selectivity so as to permit the selective recognition of one epimer over the other.

Acknowledgment. We are indebted to IVEI and DGICYT (PB90-0567) for financial support.

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[10] Compounds **3** and **4** were prepared as described by Rebek: Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476–7481. Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426–2431. Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Parris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1082–1090. For leading references to molecular receptors based on Kemp's triacid see: Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245–255.

[11] The $\Delta\delta$ for the nonequivalent methylene hydrogens permits monitoring of the conformational equilibria. For **3**, differences of 1.50 (triacid), 1.41 (monosodium salt), 1.31 (disodium salt), and 0.60 ppm (trisodium salt) are obtained (ref 9). For **4** and its mono- and dianion, differences of ca. 1.4 ppm are found for the two hydrogens of the methylene group situated between the two equivalent carboxyls, and a difference of only 0.46 ppm is found for the trianion.

[12] Potentiometric measurements were carried out in aqueous solutions at 298.15 K in 0.15 mol dm^{-3} by using equipment already described (see ref 8). The program SUPERQUAD was used to calculate the stability constants: Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195–1200. The titration curves for each system were treated as a single set or separately without significant variations in the values of the constants.

[13] MMX as implemented in PCMODEL, Serena Software, Bloomington, IN.

Corannulene Bowl-to-Bowl Inversion Is Rapid at Room Temperature

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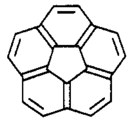
Our recent development of a convenient new route to corannulene (**1**)[1] and derivatives thereof (see below) has enabled us to measure the bowl-to-bowl inversion barrier for this archetypical curved network of trigonal carbon atoms.



1
Corannulene

The 300-MHz ^{1}H NMR spectrum of racemic corannulenyldimethylcarbinol (**2**)[2] in acetone-d_6 shows a single sharp peak for the diastereotopic methyl groups at room temperature (δ 1.87) but two well-resolved singlets at −90 °C ($\Delta\nu = 39.2$ Hz). The coalescence temperature for these two signals was found to be −64 °C (209 K), from which we calculate the barrier for bowl-to-bowl inversion in **2** to be $\Delta G^{\ddagger} = 10.2 \pm 0.2$ kcal/mol at this temperature.[3] Unless this barrier has a significant negative $\Delta S^{\ddagger}$ com-

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[†] Visiting scholar from Sharif University of Technology, Tehran, Iran.

[1] Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082–7083.

[2] Corannulenyldimethylcarbinol (**2**) was prepared in routine fashion from bromocorannulene (**4**) by sequential treatment with *n*-BuLi and acetone, all at −78 °C in THF (40% yield based on unrecovered starting material). The product (**2**) was purified by preparative TLC on silica gel (10% EtOAc–hexane): ^{1}H NMR (300 MHz, acetone-d_6) δ 8.60 (d, 1 H, $J = 9.0$ Hz, H-10), 8.07 (s, 1 H, H-2), 7.96–7.91 (m, 7 H, H-3,4,5,6,7,8,9), 1.87 (s, 6 H, CH$_3$), 1.21 (s, 1 H, OH); high-resolution mass spectrum calcd for C$_{23}$H$_{16}$O 308.1201, found 308.1209.

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