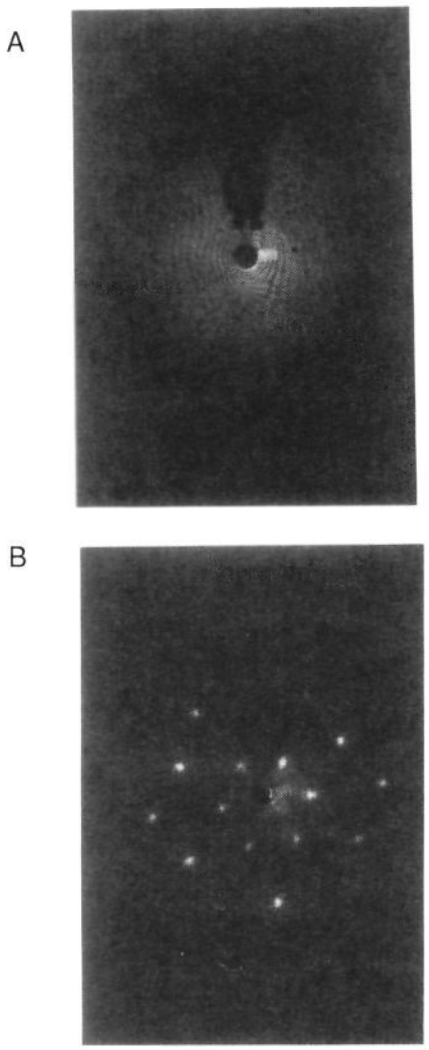

Figure 2. LEED pattern for a post-anodized Pd(111) metallic surface before (A) and after (B) exposure to 0.2 mM NaI at pH 10. Experimental conditions were as in Figure 1.

of chemisorbed I atoms. Combined analysis of the LEED and AES data suggest the formation of a Pd($\sqrt{3}\times\sqrt{3}$)$R30°$–I superlattice. The same structure is obtained whether iodine chemisorption is from gaseous or aqueous I_2 or HI.[6]

In 0.1 M NaF at pH 10, oxidation of the Pd surface starts at 0.4 V (Ag quasi-reference electrode). The oxidized surface is reduced back to the metal at −0.25 V. It is known that anodic oxidation disorders the electrode surface, presumably due to place-exchange reactions. Long-range order is not necessarily reestablished even after the oxided electrode is reduced back to the metal. Such is the case for Pd, as documented in Figure 2A by the absence of the (1×1) integral-index spots in the LEED of the post-anodized metallic surface. Figure 2B shows the LEED pattern generated when the oxidatively disordered Pd(111) electrode was immersed, at room temperature and at potentials within the double-layer region, in a solution of 0.2 mM NaI at pH 10. This LEED pattern is identical with that for the initially ordered Pd(111) electrode, Figure 1B. The Auger spectrum for the *reordered* interface is likewise identical with that for the unoxidized surface. It is thus clear that the oxidatively disrupted Pd(111) surface has been reordered by iodine chemisorption. Since the reordering occurs under conditions where Pd dissolution should be negligible, the driving force for this ordered surface reconstruction is most probably the formation of the highly stable Pd(111)($\sqrt{3}\times\sqrt{3}$)$R30°$–I superlattice.

The present results suggest that it may be possible to regenerate, in situ, clean and ordered Pd(111) electrode surfaces from the simple sequence of oxidation, reduction, and iodine chemisorption. The iodine-free single-crystal surface could then be prepared according to published procedures.[4] Further studies are aimed at (i) exploring the applicability of the iodine-chemisorption reordering method to other electrodes and (ii) identifying other reagents that can effect this in situ chemisorption-induced reordering phenomenon.

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Molecular Recognition: A Remarkably Simple Receptor for the Selective Complexation of Dicarboxylic Acids†

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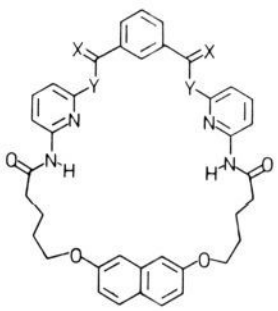
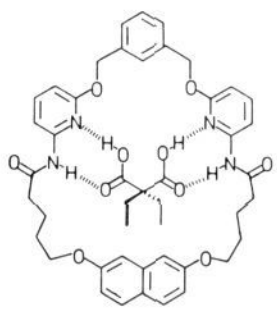
A principal theme in the design of artificial receptors has been the use of rigid molecular components to hold hydrogen-bonding groups at a fixed distance apart. Recent reports from these[4] laboratories have shown that separation of two 2,6-diaminopyridine subunits by an isophthalate spacer leads to a receptor **1** that forms strong, multi-hydrogen-bonded complexes with barbiturate and urea derivatives.[5] In this paper we report, as a further development of this approach, a novel series of receptors for dicarboxylic acids.[6]

The barbiturate receptor **1**[4] was initially modified for dicarboxylic acid complexation by replacing the two phthalamide groups by benzyl ethers, **2**. This has the effect of maintaining



1; Y = NH, X = O
2; Y = O, X = 2H



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† This paper is dedicated to the memory of Professor Matt Mertes.

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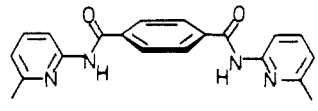
Table I

diacid	K_a, M^{-1}
adipic acid	$>10^5$
glutaric acid	$(5.9 \pm 1.6) \times 10^4$ [a]
3,3-dimethylglutaric acid	$(2.5 \pm 0.6) \times 10^4$ [a]
sebacic acid	$(3.3 \pm 0.7) \times 10^3$ [b]

[a] Determined by nonlinear regression analysis of titration data[11] at 298 K. [4] $\approx 1 \times 10^{-3}$ M; [diacids] = (0–1) $\times 10^{-2}$ M. [b] [4] = 9.8×10^{-4} M; [sebacic] = (0–7.7) $\times 10^{-4}$ M, due to insolubility of substrate.

the overall geometry of the molecule while increasing the basicity of the pyridine and reducing the hydrogen-bonding ambiguity. Receptor **2** was prepared by reaction of benzene-1,3-dimethanol with 2-bromo-6-aminopyridine (sealed tube, NaH; 37% yield)[7] followed by macrocyclization[4] with the appropriate naphthalene diacid dichloride[8] (CH_2Cl_2, Et_3N; 27% yield).[9] Titration of a $CDCl_3$ solution of **2** with diethylmalonic acid[10] gave large downfield shifts of the amide protons consistent with a tetra-hydrogen-bonded complex of type **3**. The association constants[11] for diethylmalonic acid ($(1.1 \pm 0.2) \times 10^3$ M^{-1}) and ethylmalonic acid ($(7.2 \pm 1.2) \times 10^3$ M^{-1}) are relatively small[4] and presumably reflect the unfavorable, planar conformation[12] of the diacid required for binding into the cavity, as in **3**.

A wider separation of the two hydrogen-bonding regions would both minimize repulsive interactions between the carboxylate groups and change the binding specificity to longer dicarboxylic acid substrates. Such an arrangement is achieved in a single synthetic step by the reaction of terephthaloyl dichloride with 2-amino-6-methylpyridine (THF, Et_3N) to form diamide **4**[9] in 75% yield. Molecular modelling studies[13] on **4** show the relative



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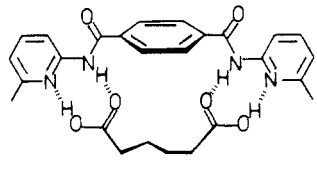
position of amide NH (~6.0 Å) and pyridine N (~10.7 Å) groups on the two picolines to be well-suited for the complexation of dicarboxylic acids separated by three or four methylene groups.

Addition of solid adipic acid to a $CDCl_3$ solution of **4**[14] led to a rapid dissolution of the normally insoluble substrate. Integration of the ^1H NMR spectrum established a 1:1 stoichiometry, and large downfield shifts (2.6 ppm) of the amide NH resonances indicated a hydrogen-bonded complex of type **5**.[15] The position



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of the alkyl chain across the face of the concave host was further

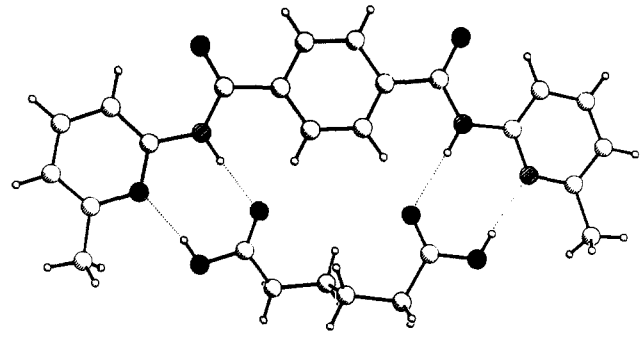

Figure 1. X-ray structure of **5**.

supported by the observation of an intermolecular NOE between the terephthaloyl protons and the protons on the two central methylenes of the adipic acid. An X-ray analysis of complex **5** (Figure 1) confirms the proposed solution structure. The benzene ring takes an edge-on orientation to the substrate, positioning its closer protons 3.28 Å from those of the 2- and 3-methylenes of the adipic acid.[16] Four hydrogen bonds are seen between the amidopicolines and the carboxylic acids, and their bond lengths of 2.9 (amide N···O) and 2.7 Å (pyridine N···O) fall in the normal range.[18] However, the acidic proton is localized on the carboxylate O (O···H, 0.86 Å; pyr N···H, 1.87 Å), showing that no proton transfer to form the carboxylate–pyridinium ion pair has occurred.[19] The neutral, tetra-hydrogen-bonded complex is, nonetheless, very stable. Dilution of **5** in $CDCl_3$ to 3×10^{-4} M caused little change in the ^1H NMR resonances of the complex, suggesting an association constant for **5** of $>10^5$ M^{-1}.

The selectivity of the receptor for adipic acid is dramatically illustrated by solid–liquid extraction experiments. Addition of a 1:1:1 mixture of diglycolic, benzene-1,4-diacetic, and adipic acids to a $CDCl_3$ solution of **4** results in the selective extraction of adipic acid into solution. A series of titration experiments were carried out with more soluble diacids, and the resulting association constants[11] are collected in Table I. Strongest complexes are formed with those diacids (adipic, glutaric) whose length and steric features correspond to the interior of the cavity. With 3,3-dimethylglutaric acid the CH_3 substituents project toward the terephthaloyl group and the resulting steric congestion leads to a drop in binding affinity. Succinic acids are too small to bridge the cavity and form 2:1 complexes with **4**. A Job's plot[20] for the complex between 2,2-dimethylsuccinic acid and **4** confirms this, showing a maximum at a mole ratio of ~0.35. However, the overlong substrate sebacic acid was shown[20] to form 1:1 complexes with **4**, but with reduced affinity.

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Supplementary Material Available: Crystallographic details for **5** including tables of atomic coordinates, thermal parameters, bond angles, and bond lengths (7 pages). Ordering information is given on any current masthead page.

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(9) All new compounds showed satisfactory spectroscopic and microanalytical and/or high-resolution mass spectral data.
(10) [2] = 2×10^{-3} M; [diacid] (0–20) $\times 10^{-3}$ M.
(11) Determined by nonlinear regression analysis of the binding isotherm using the Hostest program. Cowart, M. D.; Sucholeiki, I.; Bukownik, R. R.; Wilcox, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 6204–6210. We thank Professor Wilcox for generously providing a copy of this program.
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(14) ^1H NMR of **4** ($CDCl_3$): 8.55 (2 H, s, NH), 8.19 (2 H, d, J = 8 Hz, pyr-3H), 8.06 (4 H, s, terephth-H), 7.68 (2 H, t, J = 8 Hz, pyr-4H), 6.97 (2 H, d, J = 8 Hz, pyr-5H), 2.50 (6 H, s, CH_3).
(15) ^1H NMR of 1:1 **4**:adipic acid ($CDCl_3$): 11.13 (2 H, s, NH), 8.37 (2 H, d, J = 8 Hz, pyr-3H), 8.15 (4 H, s, terephth-H), 7.74 (2 H, t, J = 8 Hz, pyr-4H), 6.97 (2 H, d, J = 8 Hz, pyr-5H), 2.49 (m, 10 H, CH_3, CH_2CO_2H), 1.77 (4 H, m, CH_2CH_2CO).
(16) The adipic acid binds to **4** with two gauche interactions in the chain (across C_2–C_3 and C_4–C_5). This represents a significant difference from the all-trans structure seen in the X-ray structure of adipic acid[17] and demonstrates the ability of a rigid receptor to stabilize higher energy (and potentially reactive) conformations of flexible substrates.
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