Table I. Comparison of the Newly Calculated MM2 Data of BC-8 Carbon with Previous Work[a]

	ref 2	JH[b]	MM2
unit cell, Å	4.28	4.293	4.42
density, g/cm^3	4.1 (calcd)	4.03	3.68
number density, mol·atoms/cm^3	0.338	0.336	0.306
energy, kJ/mol	230[c]	142	47
A, Å	1.42	1.54 (def)	1.60
B, Å	1.23	1.54 (def)	1.49
C, Å	–	2.18	2.34
θ_1, deg	99.8	97.94	100.0
θ_2, deg	116.8	118.12	117.2

[a] See also Figure 3. [b] Refernece 3. [c] Calculated by Hoffmann.

surface atoms. The bond length for both diamond lattices is found to be 1.537 Å (experimental, 1.544 Å) and leads to a cell constant a = 3.549 Å of the unit cell of cubic diamond. The calculated density is 3.57 g/cm^3.

To ensure that the geometry of BC-8 carbon obtained from the central cage (Figure 3) is independent of surface effects, the distances A, B, and C, are calculated for each model. As can be seen in Figure 4, the corresponding values are constant in models larger than about 200 atoms.

Most important is the nonequivalence of the bond lengths A and B, which were arbitrarily assumed to be identical in the approach of Johnston and Hoffmann. According to our data, every carbon atom has one nearest neighbor at a distance of 1.49 Å and three others at 1.60 Å. The bond angles amount to $\theta_1 = 100.0°$ and $\theta_2 = 117.2°$, respectively. This results in a larger unit cell, with a = 4.42 Å and a density of 3.68 g/cm^3. Further calculated values are compared with those of Strel'nitskii[2] and JH[3] in Table I.

The geometry of BC-8 obtained from MM2 calculations is more than 90 kJ/mol lower in energy than the idealized lattice assumed previously[3] and may be helpful for a more exact calculation of electronic properties.

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Registry No. Carbon, 7440-44-0; diamond, 7782-40-3.

In Situ Chemisorption-Induced Reordering of Oxidatively Disordered Pd(111) Electrode Surfaces

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The preparation and preservation of ordered, well-defined electrode surfaces outside an ultrahigh-vacuum environment are two of the major concerns in electrochemical surface science. We suggest a new, perhaps more general, procedure for generating an ordered surface *under electrochemical conditions*. This method is based upon our observation that a stable, highly ordered superlattice is formed when a Pd(111) single-crystal electrode previously disordered by electrochemical oxidation is exposed, at room temperature and at potentials within the double-layer region, to an alkaline solution of NaI. Four methods have been suggested previously.[1-5] Three[1-3] require high-temperature treatments outside the electrochemical cell. The fourth method,[5] based upon microscopic electropolishing, may be limited only to reactive metals.

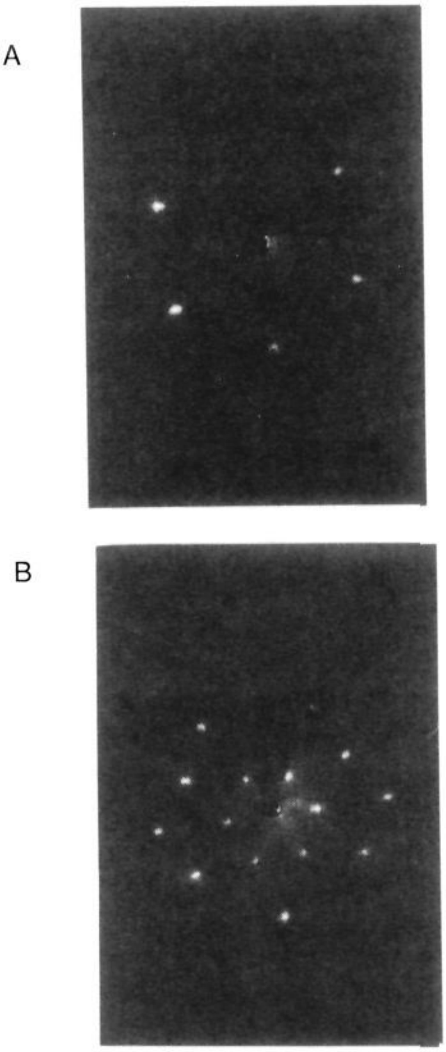

Figure 1. Low-energy electron diffraction (LEED) pattern for a clean and ordered Pd(111) single-crystal electrode before (A) and after (B) exposure to 0.2 mM NaI at pH 10. Beam energy = 60 eV; beam current = 2 μA.

Our experiments were performed in an ultrahigh-vacuum chamber equipped with low-energy electron diffraction (LEED) optics, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and an isolatable compartment for electrochemical experiments.[6] Preparation of a clean and atomically smooth Pd(111) surface was as described elsewhere.[6] Electrolytic solutions (pyrolytically triply distilled water[7]) contained 0.1 M NaF adjusted to pH 10 with NaOH. Iodine chemisorption was from 0.2 mM NaI.

Figure 1A shows the LEED pattern for a clean and ordered Pd(111) single crystal. The presence of the sharp (1×1) integral-index spots demonstrate the long-range order of the surface. The LEED pattern that results when the Pd(111) surface is exposed to dilute NaI at pH 10 is shown in Figure 1B. The distinct diffraction spots indicate the existence of a highly ordered layer

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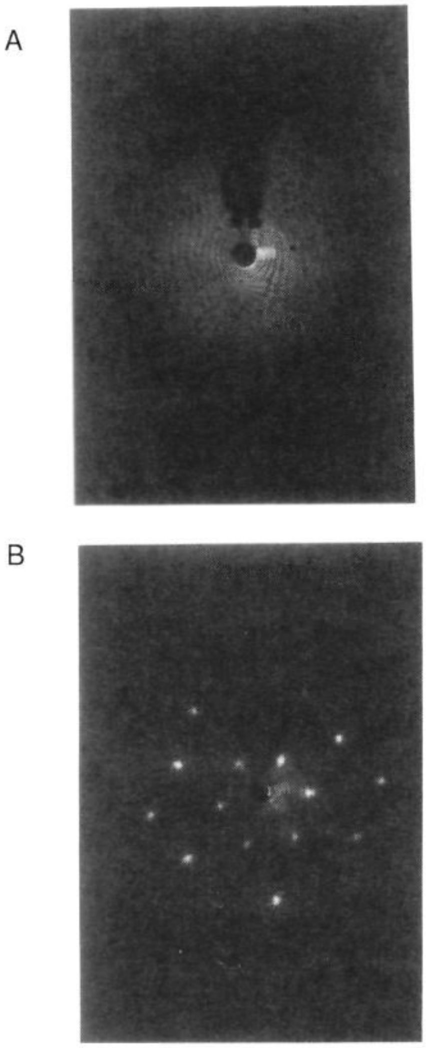

Figure 2. LEED pattern for a post-anodized Pd(111) metallic surface before (A) and after (B) exposure to 0.2 mM NaI at pH 10. Experimental conditions were as in Figure 1.

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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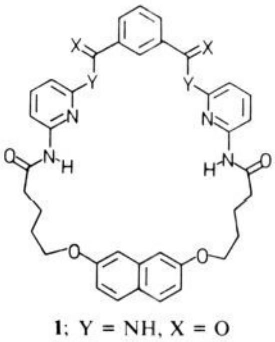
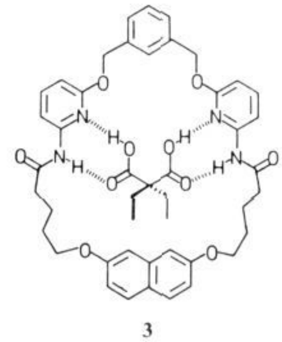
A principal theme in the design of artificial receptors has been the use of rigid molecular components to hold hydrogen-bonding groups at a fixed distance apart. Recent reports from these[4] laboratories have shown that separation of two 2,6-diaminopyridine subunits by an isophthalate spacer leads to 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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