Dipolar and Nonpolar Altitudinal Molecular Rotors Mounted on an Au(111) Surface

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Traditional interest in thermal and electric field induced molecular rotation in gases, liquids, and inside bulk solids1 has recently extended to surface-mounted2-9 and unidirectional5,10,11 rotors. Our interest in surface-mounted molecular rotors originated in the “Tinkertoy”12 concept13-15 of constructing nanosize structures and machinery by covalent binding of molecular rods and connectors. Rotors reported so far were of the azimuthal type (axle normal to the surface). Now, we describe the altitudinal (axle parallel to the surface) molecular rotors1 (nonpolar) and2 (dipolar). Such rotors may be ultimately useful, for example, in nanofluidics, electronics, and photonics.

Synthesis of the rotors 1 and 2 is outlined in Scheme 1 (formulas 1-9). Tolane dimerization16,17 with CpCo(CO)2 was extended to cross-dimerization to yield 3a. After some effort,18 Kabalka’s version19 of Suzuki coupling20 emerged as the best method for aryl-to-aryl coupling of sandwich complexes of type 3 and, specifically, for the attachment of the rotator 4 or 5 to the phenyls in 3b and 3c. Decamercuration was inspired by a prior synthesis of 10 by pentamercuration.21 It is intolerant of triple bonds, which offer lower rotational barriers, but ensures flexibility in the introduction of affinity for a surface, as any thiol will rapidly displace CF3 CO2.

The benzene planes in the rotator of 2 are calculated23 to lie at a 16° twist, left-handed (M) or right-handed (P). From dynamic 19F NMR, ΔGq(171 K) = 6.3(2) kcal/mol for M-P interconversion in 2,24 and ΔGq(182 K) = 6.7(3) kcal/mol in 11 (calculated23 Ea, 6.2 kcal/mol). Barriers to single bond rotations in 1 and 2 were too low to study by NMR; model calculations23 suggest ~3 kcal/mol. In biphenyl,25 a barrier Eb = 1.4 kcal/mol is overcome as the o-hydrogens pass each other, and another, Eb = 1.6 kcal/mol, as the rings become orthogonal. Clearly, in free 1 and 2, barriers to rotation around the rotator axle are insignificant at room temperature. The equilibrium orientation of the rotator accommodates the aryls carried by each cyclobutadiene, whose four planes are ~35° tilted17 to form a P or M propeller. The stereoisomers of 2 are MMM, MMP, MPM, and PPP, PPM, PMP, where the outside letters state the chirality of the tetraarylcyclobutadienes and the inside letter states that of the rotator.

Adsorption from solution was used to prepare monolayers and submonolayers of 1, 2 (CH2Cl2), and 10 (THF) on Au(111),26 monitored by ellipsometry,27 a quartz crystal microbalance,28 and X-ray photoelectron spectroscopy,29 which showed that over days in the open atmosphere, some of the sulfur atoms oxidize, presumably first those attached to mercury. Individual molecules in submonolayers were imaged by STM30 (Supporting Information, Figure S1) and found to be immobile over hours of scanning, both on fresh and on oxidized months-old samples. Their surface areas varied with imaging conditions and were roughly 2-3 nm2 (1 and 2) and ~2.5 nm2 (10), compatible with stretched-tentacle structures on Au(111) optimized with the molecular dynamics program TINK31 (Figure 1; in the absence of oxidation, the calculated areas are ~9 nm2 for any diastereomer of 1 and 2, and ~4 nm2 for 10). For comparison, the footprint of 1 and 2 obtained from compression isotherms on an Hg/CH3CN...
interface in an electrochemical Langmuir trough was 8.5 nm$^2$ (at 0.8 V against Ag/AgCl); 4.5 nm$^2$ was found for 10 (potential independent to 1.15 V).

Can the mounted rotors turn? The two optimized surface-mounted stretched-tentacle structures shown in Figure 1 represent conformational extremes for the MMP isomer of 2 on Au(111): A stands for conformations in which the rotator is eclipsed by one or two of the 10 tentacles, and B stands for those in which the rotator is staggered with both sets of tentacles. The drawings are similar for all three diastereomers; MMP is the most stable, MMM is 6 kcal/mol higher, and MPM is 3 kcal/mol. Molecular mechanics thus suggests that the room-temperature surface carries a variety of rotor conformations: in some, the rotator is locked parallel to the surface, and in others, it flips rapidly between orientations roughly perpendicular to the surface.

This result is compatible with the pseudo-ATR IR spectrum of a monolayer of 2 on gold, which demonstrates that $\alpha \approx 0^\circ$ for a significant fraction of the rotors. The different degree of attenuation of the intense IR peaks of the rotator, of a $[I_\text{iso}(a)]$ or b $[I_\text{iso}(b)]$ symmetry, relative to their intensity in a KBr pellet $[I_\text{iso}(a)$ or $I_\text{iso}(b)]$, combined with standard selection rules, yields an approximate average value $|\alpha| \ 45^\circ$, The vibrations were identified by comparison of the spectra of 2, 10, and 11. Their transition moment directions were assumed to be those of 11, which were deduced from its linear dichroism in stretched polyethylene. Angles $\phi$ between the transition moments of b-symmetry vibrations and the rotator axle agreed within 20–30° with the results of calculations.

If a thermally activated dipole of a rotor indeed flips between orientations pointing roughly toward or away from the surface, an imposed $\approx 10^5$ V/m electric field of an STM tip will lock its direction (if the two orientations are intrinsically equally favorable, the field will dictate the dipole direction over 99% of the time at 25 °C, using the calculated dipole moment of 11, 3.7 D). The local work function responds sensitively to the presence of a surface dipole and will be different for the two locked orientations, making them detectable by tunneling barrier height imaging (BHI). Faint differential BHI spots are seen for all rotors and on the average about two-thirds of rotors 2 on Au(111), and are assigned to induced molecular dipoles. The bright spots seen for the remaining rotors are attributed to their flipping permanent dipoles (Figure 2).

Repeated scans over a set of molecules show blinking on a time scale of tens of minutes for molecules 2 but not 1. These results are compatible with the absence and presence, respectively, of a permanent dipole in the rotator of 1 and 2, and with the availability of conformations of type A (rotator locked) and of type B (rotator free), with any given rotor sharing its time between the two types of conformation. Additional shades of brightness are presumably provided by conformational differences within type B and by the existence of three diastereomeric forms, which differ in the favored angle $\alpha$. 

**Figure 1.** Optimized representative eclipsed (A) and staggered (B) conformations of the MMP diastereomer of 2 on Au(111). A movie of panel B in AVI format is available.

**Figure 2.** Constant current mode (200 pA, 200 mV) STM (A,C) and differential BHI (B,D) images of 1 (bottom) and 2 (top) on Au(111). Six colors (black, maroon, blue, green, yellow, and white) divide equally the vertical range (left, 0–1 nm; right, 0.0–0.2 V). In STM, the molecules appear as bright yellow spots with green rims.
It would be interesting to drive the rotator flipping of 2 on Au(111) at microwave frequencies. According to molecular dynamics runs31 for B conformers, an alternating electric field perpendicular to the surface will induce unidirectional rotation in the MMP and, to a smaller degree, MPM isomers and random flipping in the MMM isomer. The directionality is due to the asymmetry of the rotational potential about the direction of the surface normal.43 A typical run for the MMP form (90 GHz, 3 × 10^{-8} V/m, 300 K) can be viewed by clicking on Figure 1B in the web edition. At low temperatures, 2 is calculated to behave as an approximately critically damped single-molecule parametric oscillator. The choice of electric field frequency and amplitude dictates the frequency of the net unidirectional rotation of its rotator, from zero to synchronous with the field, with intermediate subharmonic steps (\Omega /2, \Omega). At room temperature, stereoisomer interconversion will be rapid, and the average behavior of each rotor molecule will be bidirectional.

In summary, we have fabricated and characterized surface-mounted aldital rotors 1 and 2 on gold and have provided evidence that at room temperature the flipping of the rotator in a fraction of rotors 2 is subject to a small enough barrier to occur spontaneously and to be controllable by the electric field of an STM tip. In the MMP (and PPM) and, to a small degree, the MPM (and PMP) stereoisomers, unidirectional rotation is predicted in alternating electric field.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

References

(12) Tinkerton is a trademark of PlaySkool, Inc., Pawtucket, RI 02862, and M. Lieberman for stimulating discussions.
(24) Below ~80 °C, a weak broad signal appears at somewhat lower \delta values, presumably due to a minor diastereomer. \textsuperscript{1}H and \textsuperscript{13}C spectra do not change down to ~110 °C.
(26) Substrates were either purchased from Molecular Imaging, Inc., or prepared by thermal evaporation of gold at 1 Ås on mica that had been heated to 350 °C at 5 × 10^{-8} Torr for at least 2 h. The film was then heated to 450 °C for 30 min, allowed to cool under vacuum, and annealed with a hydrogen flame immediately before use. STM imaging showed large terraces of Au(111).
(27) Rudolph Research AutoEL instrument.
(28) QC100, Stanford Research Systems, simultaneously monitored the frequency and resistance changes of the crystal as the rotors were deposited from a ~10^{-4} M solution onto a 5 MHz, 1°, AT-cut quartz crystal with a polished gold surface.
(29) A Physical Electronics model 3800 XPS spectrometer with a hemispherical analyzer, a resistive channel electron multiplier, and a monochromatic Al K\textsubscript{α} line (1486.6 eV) X-ray source was used. Survey scans from 10 to 1000 eV were acquired with a pass energy of 187.5 eV in steps of 0.8 eV. Higher resolution spectra of Co, F, Hg, and S were obtained with a pass energy of 23.5 eV in steps of 0.1 eV.
(30) An attempt is underway to determine the abundance of bound and unbound thioether sulfur atoms, the degree of oxidation, and the likely role of Hg atoms in surface adhesion.
(31) Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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