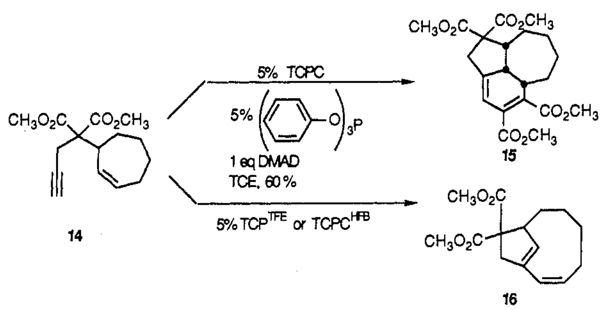

(8)

(9)

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opened a new type of reaction that has much synthetic potential and raises many intriguing mechanistic questions.

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Supplementary Material Available: Characterization data for **4** (R = CH_2CF_3), **4** (R = $CH_2CF_2CF_2CF_3$), **7** (n = 1, 2, 6, R′ = H), **7** (n = 2, R′ = CH_3), **9** (n = 1, 2, 6, R′ = H), **9** (n = 2, R′ = CH_3), and **10–16** (4 pages). Ordering information is given on any current masthead page.

Formation of a Crystalline Monolayer of Folded Molecules by Solution Self-Assembly of α,ω-Alkanedioic Acids on Silver

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The preparation of well-defined monolayers by solution self-assembly provides structures of great interest and utility for application to interface studies. Among the increasing number of applications that have been reported are fundamental wetting studies,[1] functionalized electrodes for electrochemical processes,[2-4] and templates for synthesis of organized structure multilayer films.[5,6] Most of the monolayer systems have involved alkylsiloxanes on silicon (oxide)[5,7] and gold,[3] divalent organosulfur compounds on gold,[1,2,8-11] and alkanoic acids on aluminum (oxide)[12] and silver (oxide).[13] In addition, some have displayed a marked flexibility in providing selected organic functionality at the ambient surface. This is particularly the case for the organosulfur/Au system.[14]

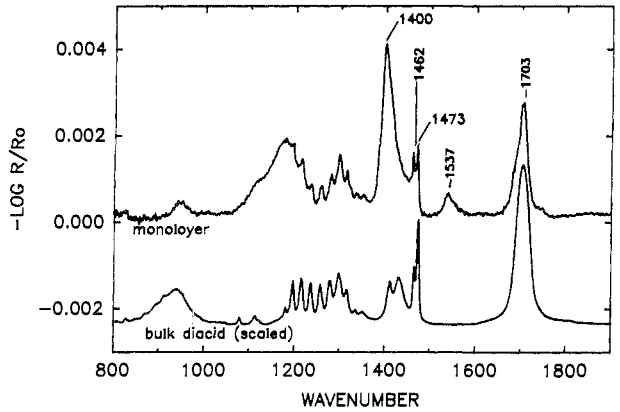

Figure 1. IR spectra of $HO_2C(CH_2)_{30}CO_2H$ after monolayer adsorption onto a Ag surface and after dispersion into a KBr pressed disk (the absorbance values have been scaled for presentation on the monolayer plot). The wavelength region from 800 to 1900 cm^{-1} is shown.

Generally, these assemblies consist of linear alkyl chains, usually highly conformationally ordered[3,8,11,13] and in some cases crystalline packed.[13,15] Since the *chains extend away from the substrate*, terminal functionality is provided. An alternative strategy for creating structured surfaces that has not yet been explored involves pinning both ends of each chain molecule to the substrate so that the chain must fold. The result is to provide *interior functionality* at the ambient interface. Such surfaces should be uniquely useful for the development of experimental model structures for biological systems as well as polymer surfaces which typically consist of chain folds.

We report here the first example of a crystalline-packed, self-assembled monolayer of a folded molecule in which *the interior of the molecule defines the ambient surface properties*. Specifically, we have observed that 1,32-dotriacontanedioic acid, $HO_2C(CH_2)_{30}CO_2H$,[16,17] adsorbed from dilute tetrahydrofuran

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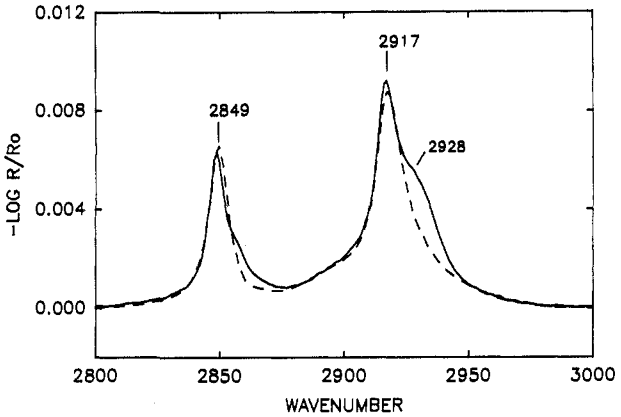

Figure 2. IR spectra of $HO_2C(CH_2)_{30}CO_2H$ after monolayer adsorption onto a Ag surface and after dispersion into a KBr pressed disk (the absorbance values have been scaled for presentation on the monolayer plot). The KBr disk spectrum is shown as a dashed line. The wavelength region from 2800 to 3000 cm^{-1} is shown.

solution at room temperature onto a freshly evaporated silver surface (on silicon substrates)[18] forms a crystalline monolayer. The monolayer structure consists of folded chains of loop shape bound by the carboxyl groups at the substrate. The evidence for this structure is based on contact angle measurements, infrared spectroscopy, and ellipsometry.

Single-wavelength ellipsometry yields an average surface film thickness of 20 ± 2 Å[19] that is precisely reproducible from spot to spot. We note that the most compact loop that can be formed by the diacid has a hairpin fold of six CH_2 groups so that the vertical extension from the substrate surface is ~22 Å, in good agreement with the measured value.

That the surface consists of CH_2 groups is shown by the pH-independent water contact angle (static pendant drop), which is observed to be 103° both for the monolayer and for clean polyethylene. This demonstrates that, since the CO_2H groups are pH sensitive, these groups reside at least 5–10 Å below the monolayer surface[9] and that this upper surface region has a CH_2 group density similar to that of polyethylene. Further, the surface is completely wetted by hexadecane, also a property of polyethylene surfaces.

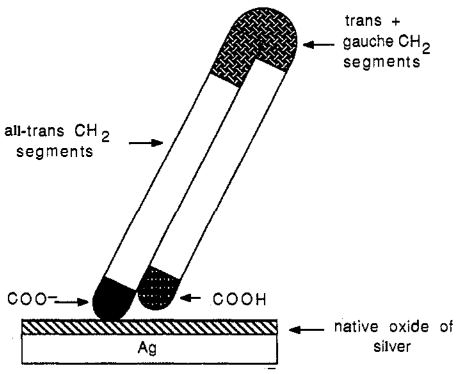

Figure 3. Pictorial representation of an isolated adsorbate molecule on a silver (oxide) surface. The structure combines features derived from the total of the characterization data. The implication of a tilt to the trans stems is deliberate (see footnote 22).

The reflection infrared (IR) spectra[20] in Figures 1 and 2 indicate a number of relevant structural features. (i) The symmetric and antisymmetric C–H stretching bands have components with frequencies at 2849 and 2917 cm^{-1} that are consistent with crystalline-packed all-trans conformationally ordered alkyl chains.[21,22] There is, however, a shoulder at the higher frequency side of the 2928-cm^{-1} band that is not present in the spectrum of a KBr dispersion of the bulk crystalline diacid, also shown in Figure 1. This shoulder indicates a component with a low degree of conformational disorder.[23] (ii) The spectrum in Figure 2 shows a well-defined doublet with components at 1462 and 1473 cm^{-1}, which can be assigned to the CH_2 bending mode.[24] This band splitting arises in crystalline alkanes from intermolecular coupling between the two chains in an orthorhombic subcell.[24] The spectrum of the bulk crystalline phase of the diacid (in a dilute KBr dispersion) in Figure 2 also shows this doublet. (iii) The intense peak centered at 1400 cm^{-1} and the weaker band at 1537 cm^{-1} are attributed to the symmetric and antisymmetric stretching modes, respectively, of a carboxylate group. Our assignment follows that reported for the 1400- and 1514-cm^{-1} bands in self-assembled monolayers of *n*-alkanoic acids on silver.[13] In general, the antisymmetric carboxylate mode is more sensitive to molecular structure and environment than the symmetric mode.[25] The frequency of the antisymmetric band for the diacid is 23 cm^{-1} higher than for the monoacid, and this suggests some differences in adsorbate attachment group structure. (iv) The band at 1703 cm^{-1} clearly belongs to the C=O stretching mode of a hydrogen-bonded CO_2H group.[25] An analogous band appears at 1703 cm^{-1} in the KBr dispersion spectrum of the diacid. Points iii and iv indicate that for this film there are two kinds of chain ends. One consists of a carboxylate species attached to the silver (oxide) surface, and a second kind consists of hydrogen-bonded CO_2H groups. We presume the fraction of each to be one-half. The CO_2H groups in the monolayer and in the bulk crystalline phase must have similar environments because their C=O stretching frequencies are identical. This suggests that the CO_2H groups in the monolayer are hydrogen bonded since this is the case for crystalline alkanoic acids.[26] Further, it is clear from the contact angle data that the CO_2H groups are well removed from the ambient, highly hydrophobic surface. (v) The series of sharp bands appearing between 1150 and 1350 cm^{-1} in Figure 1 represents a progression of wagging modes. Such a series of bands is normally associated with extended polymethylene chains.[27] It is important to note that the spacings between bands in the spectrum of the bulk crystalline phase progression bands do not exactly match those for the monolayer. The difference is such as to indicate that the all-trans sequence length in the surface film is less than that for the fully extended chain.[28]

In summary, the total of the IR evidence strongly supports a loop structure, in which crystalline-packed all-trans stems are bound to the surface by two species of carboxyl groups and which exhibits a short sequence of conformationally disordered CH_2

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(18) The Ag was deposited from a resistively heated Mo boat in a cryopumped vacuum chamber operating at a base pressure of ~2 × 10^{-8} Torr. A Cr adhesion promotion layer of ~125 Å was first deposited on the Si. Cross-section TEM examination of the sample indicates flat regions ~50 mm across and ~2 nm high with defect regions (grain boundaries) ~2 nm across. The deposition procedure essentially follows that reported previously for gold films (ref 8).

(19) The measurements were made a Rudolph Auto-El null instrument operating at 632.8 nm with a 70° angle of incidence. The thickness calculations were performed by using a film refractive index of 1.47 according to a previously established procedure (ref 12).

(20) Infrared spectra were obtained at 2-cm^{-1} resolution by a single reflection of a p-polarized beam at an 86° angle of incidence using a modified Digilab 60 Fourier transform spectrometer bench. Details of the instrumentation and exact measurement procedures have been reported elsewhere (ref 12). The quantity R/R_0 is derived from a measurement of the reflectivity spectrum of the sample (R) and of a "clean" blank gold film (R_0) (see ref 12).

(21) For example, see: MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, *88*, 334–341.

(22) The fact that the intensity of these spectral components is not 0 means that the planes of the all-trans CH_2 groups are tilted away from being parallel to the surface (see discussions in refs 8 and 11–13), indicating a tilt to the chains away from perpendicular to the surface. The exact tilt can be calculated from the spectra, and preliminary analysis indicates an average value in the range of 20–30°.

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groups at the ambient side of the monolayer. A pictorial structure of an isolated adsorbate molecule that incorporates features consistent with our data is given in Figure 3. Recent measurements on a monolayer consisting of a diacid with a $(CD_2)_6$ segment at the center of the chain demonstrate that the fold must consist of at least six methylene groups.[28] These experiments, additional ones involving more complex folded molecular structures, and further characterization of the ordering in such structures will be reported in detail in future publications.

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Registry No. Ag, 7440-22-4; $HO_2C(CH_2)_{30}CO_2H$, 14604-28-5.

Principle of Maximum Hardness

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From his considerable experience with the concepts of chemical hardness and softness, in 1987 Ralph Pearson concluded that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible."[1] Subsequent studies of particular problems support this principle and imply that its validity may require conditions of constant temperature and chemical potential.[2] Following is a formal proof of the principle, as so modified.

Absolute hardness η and absolute softness S, of the equilibrium state of an electronic system at temperature T, are defined by

$$2\eta = \left(\frac{\partial\mu}{\partial N}\right)_{v(\mathbf{r}),T} \quad \text{and} \quad S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial\mu}\right)_{v(\mathbf{r}),T} \qquad (1)$$

where μ is the electronic chemical potential (constant through the system),[3] N is the number of electrons, and $v(\mathbf{r})$ is the potential acting on an electron at $\mathbf{r}$ due to the nuclear attraction plus such other external forces as may be present. These definitions are the finite-temperature extensions of the ground-state definitions of these quantities.[4-6] The chemical potential is the Lagrange multiplier for the normalization constraint in the finite-temperature density-functional theory.[6,7] It also is the negative of the absolute electronegativity.[3] In terms of the Helmholtz free energy, $\mu = (\partial A/\partial N)_{v(\mathbf{r}),T}$. Note that $v(\mathbf{r})$ constant implies total volume constant.

Imagine a grand canonical ensemble consisting of a large number of perfect replicas of a particular electronic system of interest, in equilibrium with a bath at temperature T and chemical potential μ, with the bath also controlling $v(\mathbf{r})$. The members of the ensemble may exchange energy and electrons with each other. Equilibrium averages being denoted with brackets, N will fluctuate about $\langle N\rangle$. The equilibrium softness is given by[5]

$$\langle S\rangle = \left[\frac{\partial\langle N\rangle}{\partial\mu}\right]_{v(\mathbf{r}),T} = \beta\langle(N - \langle N\rangle)^2\rangle \qquad (2)$$

where $\beta = 1/kT$. Or,

$$\langle S\rangle = \beta\sum_{N,i} P^0_{N,i}(N - \langle N\rangle)^2 \qquad (3)$$

where

$$P^0_{N,i} = (1/\Xi)\exp[-\beta(E_{Ni} - N\mu)] \qquad (4)$$

and

$$\Xi = \sum_{N,i}\exp[-\beta(E_{Ni} - N\mu)] \qquad (5)$$

Ξ is the grand partition function. The probabilities $P^0_{N,i}$ define the equilibrium distribution. They are functions of the parameters that characterize the ensemble: β, μ, and $v(\mathbf{r})$; dependence on $v(\mathbf{r})$ comes through the fact that the E_{Ni} depend on $v(\mathbf{r})$.

Now consider the countless other, nonequilibrium ensembles of the same system of interest, at temperature T but characterized by probabilities $P_{N,i}$ different from the canonical probabilities $P^0_{N,i}$. An average in any such ensemble may be denoted with overbars, as for example $\bar{S} = \beta\sum_{N,i}P_{N,i}(N - \langle N\rangle)^2$. Consider only those of these nonequilibrium ensembles that can be generated as equilibrium ensembles by changing the bath parameters μ and $v(\mathbf{r})$, by small amounts. For any one of these, it will be shown that

$$\bar{S} - \langle S\rangle = \beta\sum_{N,i}(N - \langle N\rangle)^2(P_{N,i} - P^0_{N,i}) \geq 0 \qquad (6)$$

Consequently, among all these states, the equilibrium state may be characterized as having minimum softness.

Proof of eq 6 follows from the fluctuation–dissipation theorem of statistical mechanics.[8] For simplicity employing classical statistical mechanics, let the equilibrium probability distribution function for the system of interest, with grand potential $\Omega(\mathbf{r}^N,\mathbf{p}^N) = H(\mathbf{r}^N,\mathbf{p}^N) - \mu N$, be $f(\mathbf{r}^N,\mathbf{p}^N)$ (corresponding to $P^0_{N,i}$) and let the corresponding arbitrary nearby distribution be $F(\mathbf{r}^N,\mathbf{p}^N)$ (corresponding to $P_{N,i}$). Then the physical perturbation $\Delta\Omega(\mathbf{r}^N,\mathbf{p}^N)$ generating F at time $t = 0$ must satisfy

$$F(\mathbf{r}^N,\mathbf{p}^N) = \frac{\exp(-\beta\Delta\Omega)}{\langle\exp(-\beta\Delta\Omega)\rangle}f(\mathbf{r}^N,\mathbf{p}^N) \qquad (7)$$

$$= \langle A\rangle^{-1}A(\mathbf{r}^N,\mathbf{p}^N)\,f(\mathbf{r}^N,\mathbf{p}^N) \qquad (8)$$

where

$$CA(\mathbf{r}^N,\mathbf{p}^N) = \exp(-\beta\Delta\Omega) \quad \text{and} \quad \Delta\Omega = -\left(\frac{1}{\beta}\right)\ln\,[CA(\mathbf{r}^N,\mathbf{p}^N)] \qquad (9)$$

$f(\mathbf{r}^N,\mathbf{p}^N)$ and $\langle A\rangle$ are independent of time, and C is a positive constant serving the purpose of a field component of the perturbation which couples with A; other quantities depend on time. Equation 8 shows that the conditions are satisfied for Exercise 8.3, p 242, of ref 8. Accordingly, it follows that

$$\langle A\rangle[\bar{A}(t) - \langle A\rangle] = \langle(A(0) - \langle A\rangle)(A(t) - \langle A\rangle)\rangle \qquad (10)$$

and

$$\bar{A}(0) - \langle A\rangle = \langle A\rangle^{-1}\langle(A(0) - \langle A\rangle)^2\rangle \qquad (11)$$

Here $\bar{A}(t)$ is the average of $A(t)$ for the nonequilibrium distribution F. Now take A to be the observable that is the softness,

$$A = \beta(N - \langle N\rangle)^2 \qquad (12)$$

Since this $\langle A\rangle$ is positive, eq 11 implies

$$\bar{S}(0) - \langle S\rangle \geq 0 \qquad (13)$$

which is the inequality of eq 6.

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