Effect of Biphenyl and Naphthyl Groups on the Structure of Self-Assembled Monolayers: Packing, Orientation, and Wetting Properties

Yu-Tai Tao,* Mong-Tung Lee, and Shun-Chi Chang

Contribution from the Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

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Abstract: The self-assembling behavior of a series of 4-alkoxybiphenyl-4′-carboxylic acid and 6-alkoxy-2-naphthoic acid compounds on the surfaces of Ag and Cu was studied. The structure of the monolayer film was probed with ellipsometry, reflection absorption IR spectroscopy, and contact angle measurements. The effect of aromatic chromophores on the packing, orientation of the molecular assembly, and wetting properties of the monolayer film was investigated. These monolayer structures were compared with those of *n*-alkanoic acids and *n*-alkanethiols to deduce the packing mechanism of carboxylic acid adsorption on metal oxides.

Introduction

The understanding of parameters that determine the structure of self-assembled monolayers (SAMs)[1] on solid surfaces is of fundamental importance in molecular engineering utilizing these monolayers. The extensive structural studies[2-12] carried out on alkanethiol monolayers have indicated the importance of substrate lattice in determining the structural aspects such as packing density and molecular chain orientation. For example, *n*-alkanethiol forms an epitaxial ($\sqrt{3}\times\sqrt{3}$)R30° overlayer on Au(111)[8] surface, exhibiting a chain tilt of ~27° from surface normal, while similar monolayers formed on GaAs(100) surfaces give a chain tilt of ~57°, presumably because of the widely different lattice spacing of the substrate of GaAs(111).[9] It is generally believed that a larger chain tilt results from larger lattice spacing. The silver surface has a substrate lattice that is nearly identical to that of Au (2.89 and 2.88 Å, respectively[13]), yet the structures of self-assembled *n*-alkanethiol monolayers on these two metal surfaces are quite different. The lattice of the adsorbed overlayer on silver was found to be incommensurate and rotate with respect to the Ag surface lattice.[12] The lattice spacing is smaller, and the molecular chains are nearly perpendicularly aligned.[14] The origin of the different binding lattice is controvertial,[7,8,15] although a different binding lattice was also found for sulfur[16] as well as CH_3SH[17] monolayers on Ag(111), i.e., a($\sqrt{7}\times\sqrt{7}$)R10.9° overlayer. Recently we described the structural comparison of SAMs of *n*-alkanoic acids on metal oxide surfaces.[18] It was suggested that the ultimate structure of a monolayer is a compromise between the carboxylate head group binding geometry and interchain interactions. The binding geometry in turn is related to the strength of the interaction between the head group and the substrate. On surfaces where binding interaction is dominant and binding sites are specific, the chain tilts in accordance with the binding geometry (e.g. in the case of silver) and binding lattice. Our result was in good agreement with the latest X-ray diffraction study of the SAM of docosanoic acid on Ag(111), which suggests an epitaxial film with an in-plane structure of *p*(2×2) and the molecular chain tilted at 27 ± 1° toward the nearest neighbor.[19] On surfaces where binding interaction is weaker or nonspecific, normal orientation due to optimal chain–chain interaction[20] is favored. A tilted binding geometry and twisted or bent segment near the head group may develop (e.g. in the case of copper and aluminum[18,21]).

The effect of perturbation in the otherwise linear polymethylene chain has also been studied. The assembling behavior of amphiphiles containing large size chromophores such as a phenoxy group or phenylsulfonyl group in the middle of a long chain was reported by Ulman et al.[22-25] Depending on the location of the chromophore, some disorder may be introduced into the assembly. Recently, Ulman further addressed the importance of commensurability between *strata* of closely packed atomic or chain groups

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[15] A restructured binding overlayer[8] or multidomain system[7] has been proposed to interpret the difference. A combination of three-fold hallow site and on-top site to explain the higher coverage and thus lower tilt on the Ag surface was proposed by Ulman: *Proceedings of the 6th International Conference on Organized Molecular Thin Films*; Elsevier: Sequoia, SA, 1993.

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(including the stratum of perturbing units) in determining the ordering and packing of molecular assemblies.[26]

In this paper we wish to report our study of the self-assembling behavior of a series of acid derivatives, 4-alkoxybiphenyl-4′-carboxylic acids, $CH_3(CH_2)_mOC_6H_4C_6H_4COOH$ (**I**), and 6-alkoxy-2-naphthoic acids, $CH_3(CH_2)_mOC_{10}H_6COOH$ (**II**) ($m = 15$–19), on the surfaces of Ag and Cu and to compare the results with those for monolayer systems derived from *n*-alkanoic acids, $CH_3(CH_2)_{m-1}COOH$ (**III**). The well-studied monolayers of *n*-alkanethiols, $CH_3(CH_2)_mSH$ (**IV**) were also included as a "reference" system of little chain tilt. The introduction of biphenyl and naphthyl groups into the otherwise linear hydrocarbon chain was aimed at changing the steric requirement in the packing of the molecular assembly. The aromatic chromophore next to the carboxyl group imposes a size constraint on the closeness that the neighboring head groups (or the larger "effective" head group) can approach or arrange with respect to each other. Silver and copper were chosen because our previous results show that the structures of a typical *n*-alkanoic acid on these two metals are clearly different, probably due to different binding strength, binding geometry, or site specificity. It is interesting to see how the monolayer structures respond to the perturbation introduced in the two cases. The results may aid the understanding of self-assembling mechanisms in general.

Experimental Section

Materials. *n*-Hexadecane used in preparing the adsorbing solution was obtained from Aldrich and was percolated through neutral alumina (activity 1 from Merck) twice. The series of compounds **I** were prepared from 4-hydroxybiphenyl-4′-carboxylic acid (obtained from Tokyo Chemical Inc.) via alkylation of the hydroxy group with alkyl bromides according to a literature procedure.[27] The compound **II** series were prepared similarly from 6-hydroxy-2-naphthoic acid (obtained from Tokyo Chemical Inc.). All of these compounds were purified by multiple recrystallizations from acetic acid and gave satisfactory NMR and IR data. Silver and copper used for substrates were obtained from Johnson Matthey Electronics and were of 99.99% purity or higher. Single crystal silicon wafers (2-in. diameter) polished on one side were obtained from Semiconductor Processing Co., Boston, MA.

Substrate Preparation: The substrates were prepared by thermally evaporating (at a rate of ~30 Å/s at 3×10^{-7} torr using a Ulvac cryopumped evaporator) around 2000 Å of silver or copper on to the surface of a 2-in. silicon wafer. An adhesion layer of chromium (~100 Å) was needed in the case of silver. After the substrates returned to room temperature, the vacuum chamber was back-filled with high purity nitrogen. The substrates were transferred to tightly capped wafer containers, and substrate constants were measured immediately. The substrates were placed in the acid solution immediately after the measurement. The metal surfaces were exposed to the ambient atmosphere for no more than 10 min. To minimize the effect of different ambient exposures, batches of substrates were always freshly prepared and adsorptions of compounds in the same series done at the same time.

Monolayer Preparation. Compound **I** (or **II**) was dissolved in a mixture of *n*-hexadecane and THF (1:1, v/v) at a concentration of 0.25 mM and kept at 25 °C. Substrate wafers were placed in the solution for 1–3 h before being taken out for characterization. The surfaces usually emerged dry and clean, and such surfaces were characterized as it is (with the back side and edge wiped dry with a hexane-soaked tissue). Both IR and ellipsometry showed that a quick rinsing with THF on a spinner does not change the structure of the film adsorbed on Ag. But rinsing with solvent was avoided to assure intact film structure. For substrates emerged wet from adsorbing solution (these are mainly the cases for compound **II** adsorbed on Cu), rinsing with THF was necessary to remove excessive adsorbing solution before characterization. Prolonged treatment (more than 3 h) of wafers in adsorbing solution results in a sample surface with tiny wet spots left on it, probably due to the corrosion effect of acid on the metal oxide surface. The corrosion process is faster and more serious on copper than on silver.[28] The preparation of monolayers of **III** and **IV** was reported before.[8,18]

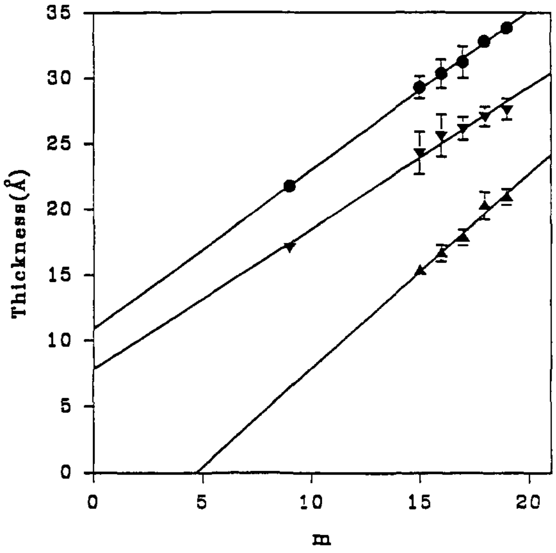

Figure 1. Ellipsometric thickness as a function of chain length (or tail group length) for monolayer on silver: ●, $CH_3(CH_2)_mOC_6H_4C_6H_4COOH$ (**I**); ▼, $CH_3(CH_2)_mOC_{10}H_6COOH$ (**II**); ▲, $CH_3(CH_2)_{m-1}COOH$ (**III**).

Infrared Measurement. Reflection absorption IR spectra were taken with a Bomem MB-100 spectrometer equipped with an MCT detector. A custom-designed optics system similar to that described in the literature[21] with an 86° incidence angle using p-polarization was employed. A clean gold-coated wafer was used as reference for all spectra. A monolayer of perdeuterated docosanethiol on gold was used to check the cleaniness of the reference. One thousand scans were collected at 2-cm^{-1} resolution for signal averaging.

Contact Angle measurement. Static contact angles were measured with a Rame-Hart NRL Model 100 goniometer. At least three drops of wetting liquid were measured for each sample, and the reported contact angle readings are the mean values from more than three batches of samples. The error in the hexadecane and bicyclohexyl contact angles is ~1°, while the error in the water contact angle value is ~2°.

Ellipsometry Measurement. A Rudolph AutoEL Ellipsometer was used for the thickness measurement. The He–Ne laser (632.8 nm) light fell at 70° on the sample and reflected into the analyzer. Data were taken over 3–5 spots on a given sample and averaged. A real index of refraction of 1.47 was assumed for all the films in the thickness calculation.

Results

The results were described according to the substrate metal as follows:

Silver Surface. Compound **I** with $m = 9$ and 15–19 formed an oleophobic monolayer on the Ag surface within seconds after immersion in the solution. The ellipsometric readings remained constant after 10 min of immersion. The sample was nevertheless allowed to stand in solution for 1–3 h to ensure completion without a corrosion problem.[28] The ellipsometric thickness for the series of compounds was plotted against tail group length in Figure 1. A linear correlation of the measured thickness with the chain length of the alkoxy tail group was observed, with a slope of 1.21 Å and an intercept of 11 Å. Note that all these monolayers have the same biphenylcarboxylate group as the lower portion. The intercept agrees well with the calculated thickness of 12 Å for a perpendicularly oriented 4-hydroxybiphenyl-4′-carboxylate ($m = 0$) moiety. The slope is somewhat lower than that expected for a chain standing normal to the surface, 1.26 Å per CH_2.

Reflection–absorption IR of these films are shown in Figures 2 and 3. In the low-frequency region, the monolayer spectra are nearly identical for derivatives with tail groups of different chain lengths, a representative of which ($m = 15$) is shown in Figure 2a. The transmission spectrum of the isotropic free acid is also shown (Figure 2b) for comparison. Complete dissociation of the acid on the silver surface was indicated by the absence of absorption due to free acid around 1686 cm^{-1} and the new and

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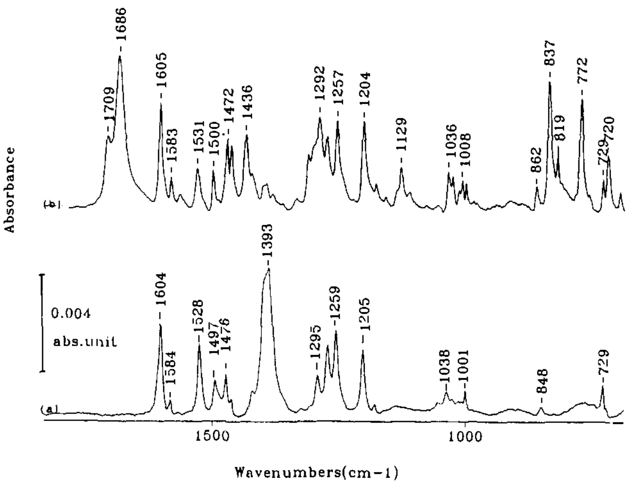

Figure 2. Low-frequency region of IR spectra for (a) monolayer of I on silver, *m* = 15, and (b) transmission spectrum of isotropic free acid of I.

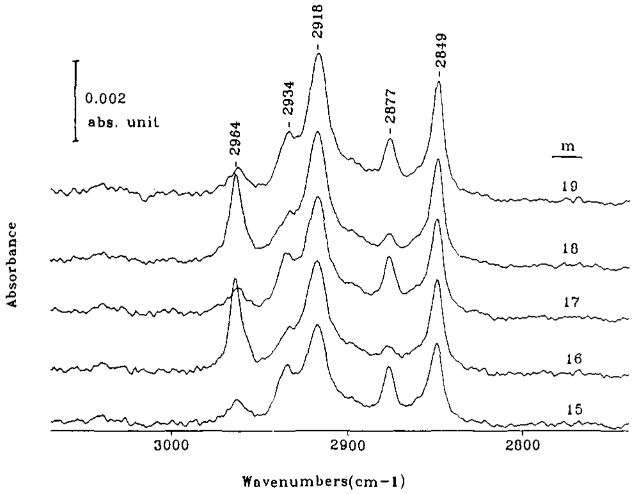

Figure 3. High-frequency region of IR spectra for monolayer of I on silver.

dominant peak at 1393 cm^{-1}, which is assigned as the symmetric stretch for the carboxylate group $\nu_s(CO_2^-)$. No new peaks appeared in region where the asymmetric stretch $\nu_a(CO_2^-)$ usually occurs.[29] This observation is similar to that displayed by *n*-alkanoic acid adsorbed on Ag, and it suggests a symmetric binding of the carboxyl group to the surface. The presence of strong peaks at 1604 and 1584 cm^{-1} (assigned as the skeletal C=C stretching vibration for the benzene ring[30,31])and1205 and 1037 cm^{-1} (assigned as the in-plane C–H bending[30,31]) excludes a parallel orientation of the aromatic nucleus on the surface.[32] A distinct difference between the isotropic sample and the monolayer spectrum is the disappearance of the out-of-plane C–H deformation modes at 837 and 772 cm^{-1} in the spectrum of the monolayer. As the out-of-plane C–H deformation has its transition dipole perpendicular to the aromatic ring, this observation lends further support to the assertion that the biphenyl group aligns virtually perpendicularly on the surface. The peaks at 1258 and 1130 cm^{-1} in the isotropic sample are assigned as the asymmetric and symmetric vibrations for the ether linkage C–O–C.[31] In the monolayer spectrum, the asymmetric stretch remains strong while the symmetric stretch disappears, presumably also due to the orientation effect (see discussion later). The absorption at 729 cm^{-1} is assigned as the rocking mode of the CH_2 units. This band is characteristic of long chain hydrocarbons with more than four methylene units.[30] In the high frequency range (Figure 3), the peak frequencies for the methylene stretches $\nu_a(CH_2)$ and $\nu_s(CH_2)$ at 2918 and 2849 cm^{-1}, respectively, are indicative of a crystalline-like monolayer.[2,33] The intensity shows a linear correlation with chain length. Figure 4 shows the intensity of $\nu_s(CH_2)$ (which is well separated from other peaks) plotted against the chain length of the tail group. The methyl vibration modes, however, show a distinct odd–even variation pattern. Even chain derivatives gave a much stronger symmetric mode $\nu_s(CH_3,FR)$ (the lower energy peak for a Fermi resonance coupler) at 2877 cm^{-1} and a weaker asymmetric mode $\nu_a(CH_3)$ at 2964 cm^{-1}. The odd chain derivatives behave just the opposite. Figure 5 plots the intensities of $\nu_a(CH_3)$ and $\nu_s(CH_3)$ as a function of chain length, together with data from other systems (see below).

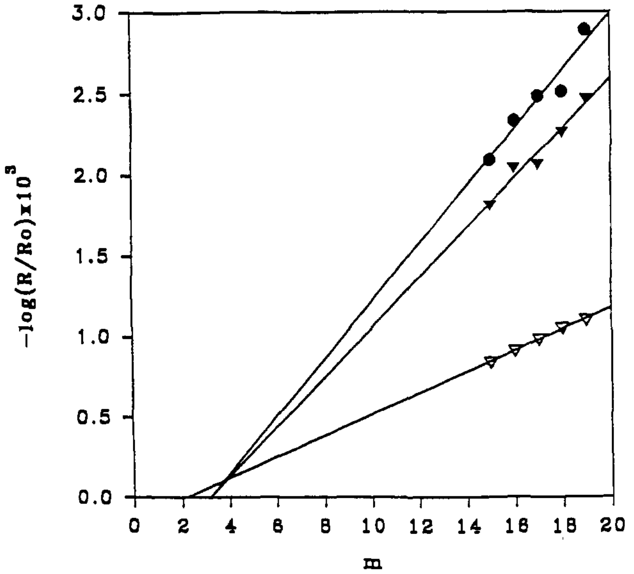

Figure 4. Intensity of symmetric CH_2 vibration mode as a function of tail group length: ●, I; ▼, II; ▽, III.

Static contact angles of hexadecane (HD), bicyclohexyl (BCH), and water were measured on the series of monolayer surfaces. A significant odd–even effect was observed for both θ_{HD} and θ_{BCH}. For the even chain derivatives (*m* = 15, 17, 19), θ_{HD} remains nearly constant at 54 ± 1°, whereas the odd chain derivatives exhibit θ_{HD} at 43 ± 1°. The θ_{BCH} values alternate between 61° and 54°, again higher on even chain derivatives and lower on odd chain derivatives. The water contact angle θ_{H_2O}, however, appears to be insensitive to the chain length difference, at 110 ± 2°. The contact angle variation is plotted as a function of chain length in Figure 6.

Compound II with *m* = 10 and 15–19also formed oleophobic monolayers on Ag. The correlation of ellipsometric thickness with the length of the tail group is also included in Figure 1. A slope of 1.07 Å and an intercept of 7.8 Å were obtained from the linear correlation. The expected thickness for a perpendicularly aligned 6-hydroxy-2-naphthoic acid (*m* = 0) binding symmetrically via carboxylate is 7.5 Å.

The reflection–absorption spectra for SAMs of II on Ag are shown in Figures 7 and 8. The transmission spectrum of the isotropic crystalline acid sample was included in the low-frequency region (Figure 7b), for comparison. Complete dissociation of the acid was also observed. The peak at 1392 cm^{-1} was assigned

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[29] The $\nu_a(CO_2^-)$ for the sodium salt of I is around 1540 cm^{-1}. The $\nu_a(CO_2^-)$ for the bulk Ag carboxylate salt is around 1515 cm^{-1}: Porter, M. D. Private communication. Peaks around this region and lower regions are attributable to the aromatic chromophore.

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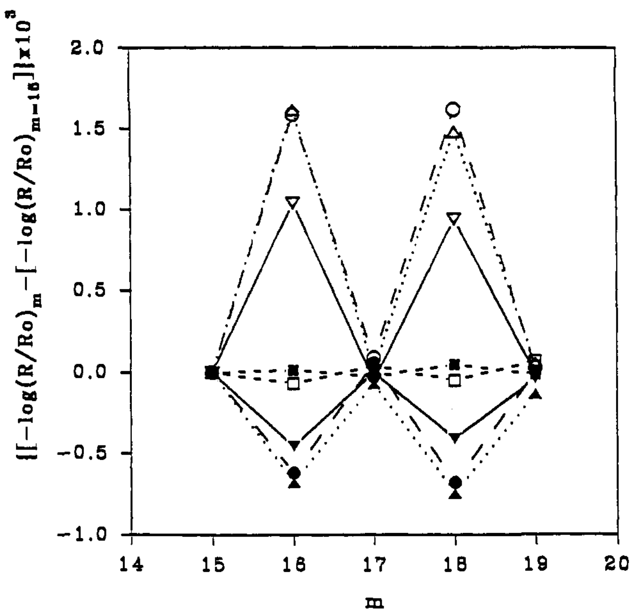

Figure 5. Intensity of methyl vibration modes as a function of tail group length. Open symbols represent $\nu_a(CH_3)$, filled symbols represent $\nu_s(CH_3)$: ■, □, IV on Ag; ▼, ▽, III on Ag; ●, ○, I on Ag; ▲, △, II on Ag.

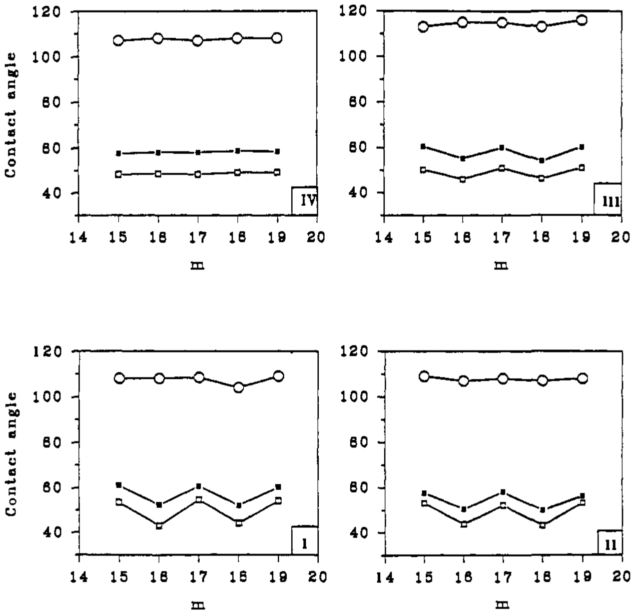

Figure 6. Contact angle as a function of chain length on monolayers of I, II, III, and IV. Wetting liquid: ○, H_2O; ■, bicyclohexyl; □, hexadecane.

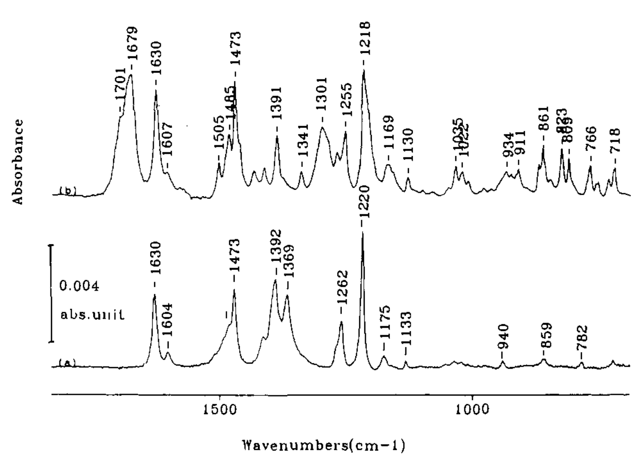

Figure 7. Low-frequency region of IR spectra for (a) monolayer of II on silver, *m* = 15, and (b) transmission spectrum of isotropic free acid of II.

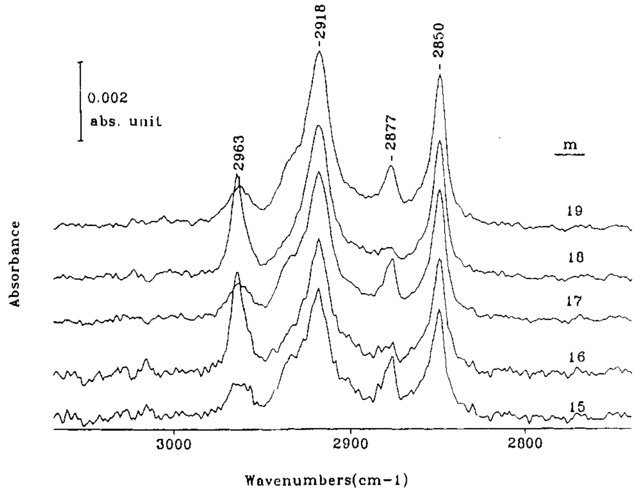

Figure 8. High-frequency region of IR spectra for monolayer of II on silver.

as the symmetric stretch for the carboxylate group, $\nu_s(CO_2^-)$. The intensity is smaller than those of the corresponding peaks in *n*-alkanoic acid and the biphenyl systems. A broad shoulder around 1485 cm^{-1} was observed near the CH_2 bending vibration at 1473 cm^{-1}. The shape is clearly different from that of the distinct peaks which were also present in this region in the isotropic sample (1485 and 1505 cm^{-1}). The frequency of the $\nu_a(CO_2^-)$ mode could also be in this region. The peaks at 1630 and 1604 cm^{-1} are assigned as the C=C skeletal stretch vibrations. The most prominant peak in the low-frequency region is the peak at 1220 cm^{-1}, which was assigned as the in-plane C–H bending mode.[30] The out-of-plane deformation modes at 861, 824, and 809 cm^{-1} which are present in the isotropic sample also become weak or disappear in the monolayer spectrum. It is inferred from these data that the aromatic nucleus orients nearly perpendicularly to the surface.[34] In the high-frequency region (Figure 8), a very similar pattern to the case of the biphenyl derivative was observed. The peak positions for the methylene stretches (2918 and 2850 cm^{-1}) indicate a well-ordered molecular chain packing. And the intensity of $\nu_s(CH_2)$ as a function of the tail group length was included in Figure 4. The relative intensities of the methyl vibration modes strongly depend on the chain length. The $\nu_s(CH_3,FR)$ mode at 2877 cm^{-1} is weak for an odd chain tail group and stronger for even-chain derivatives. The $\nu_a(CH_3)$ mode is much stronger for odd chain derivatives and smaller for even chain derivatives. The intensity variation was also plotted in Figure 5. It is noted that the variation trace more or less coincides with that for the biphenyl system.

The contact angle behavior was also plotted in Figure 6. Water contact angles appear to be rather insensitive to the chain length of these films, being around 110°. The hexadecane contact angle values θ_{HD} again show a dependence on the chain length, being 53 ± 1° on even chain derivatives and 43 ± 1° on odd chain derivatives. A parallel behavior was observed when bicyclohexyl was used as the wetting liquid, with θ_{BCH} alternating between 58° and 50°. The θ_{H_2O} remains around 109 ± 2°.

Copper Surface. Compound I also formed an oleophobic monolayer within seconds on the copper substrate upon immersion in the adsorbing solution. However, due to the oxidation process of the copper surface, meaningful measurement of the film thickness was difficult because the substrate constant changed rapidly during ellipsometric measurement. This has been observed before.[8,18] The monolayer character was nevertheless judged from

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[34] Raman spectra showed that the parent moiety, 2-naphthoic acid, gave a "standing up" orientation on colloidal Ag at high surface concentration: Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526–5530.

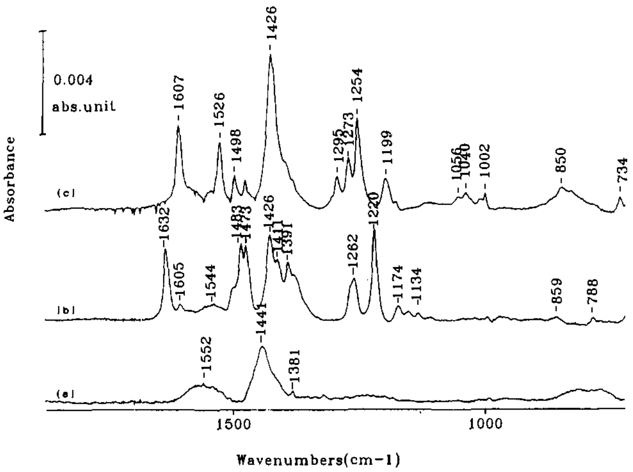

Figure 9. Low-frequency region of IR spectra for (a) monolayer of III on copper, $m = 15$, (b) monolayer of II on copper, $m = 15$, and (c) monolayer of I on copper.

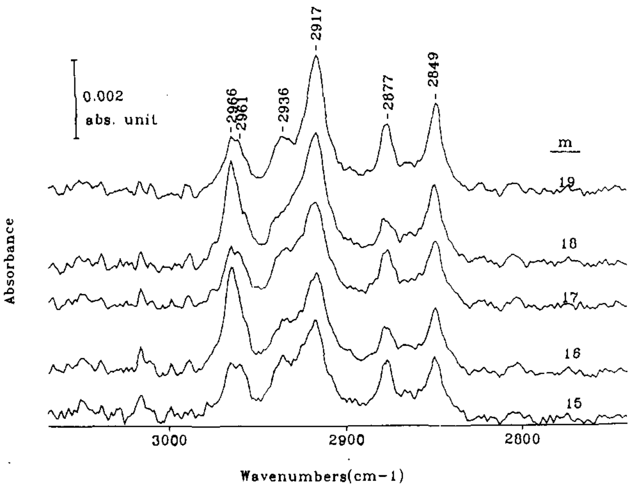

Figure 10. High-frequency region of IR spectra of I on copper.

wetting property and reflection–absorption IR results. The IR spectra of the monolayers for this series of compounds are shown in Figures 9 and 10. Also included in Figure 9 are the representative spectra for compounds II and III. The most prominant peak in Figure 9c is the peak at 1426 cm^{-1}, which is assigned as $\nu_s(CO_2^-)$. Comparison of this spectrum with the corresponding spectrum on silver (Figure 2a) indicates a broad hump rising above base line in the region around 1550 cm^{-1}, where the $\nu_a(CO_2^-)$ may occur. But the relative intensity of $\nu_a(CO_2^-)$ versus $\nu_s(CO_2^-)$ is much smaller than that observed for the *n*-alkanoic acid monolayer on Cu (Figure 9a). The rest of the features (for aromatic modes) are quite similar to that observed for the same monolayer on silver. The high-frequecy region shown in Figure 10 again indicates well ordered hydrocarbon chain packing. There is also an odd–even effect in the intensities of methyl vibration modes, whereas the amplitude of variation is clearly smaller than that observed for the same monolayer on the Ag surface. This is in sharp contrast with the case of the *n*-alkanoic acid monolayer on copper, where no odd–even alternation in methyl modes was observed (see ref 18). It is also noted that a splitting of the asymmetric methyl vibration was observed only for even chain derivatives (always occurs in many runs and thus should not be noise). These are assigned as the in-plane and out-of-plane modes $\nu_a(CH_3,ip)$ and $\nu_a(CH_3,op)$, respectively.[35]

Contact angle measurements on the series of monolayers also give an odd–even alternation when hydrocarbon liquid was used as the wetting liquid. θ_{HD} is higher on even chain derivatives at 50 ± 1° and lower on odd chain derivatives at 44 ± 1°. θ_{BCH} alternates between 55° and 51°, again in contrast with the constant contact angle on the *n*-alkanoic acid monolayer on Cu. The amplitude of variation is also smaller than that observed for I on Ag.

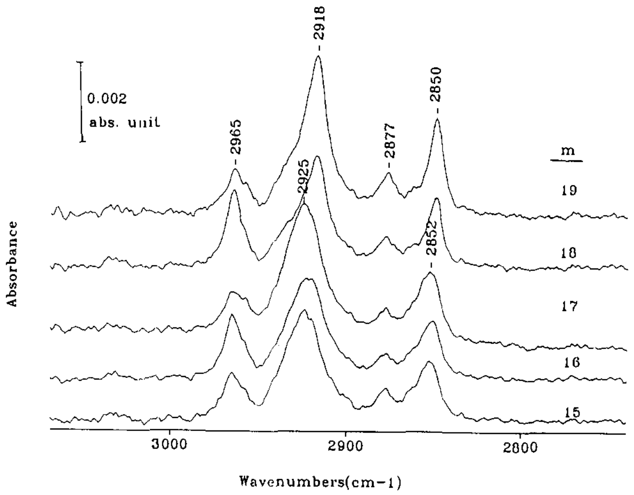

Figure 11. High-frequency region of IR spectra of II on copper.

Compound II hardly forms an oleophobic monolayer under standard conditions. After the excess solution on the surface is rinsed off with THF, the IR indicates disordered chain conformation as shown in the high-frequency region spectum (Figure 11). Methylene modes have shifted to higher frequencies. There were times when an oleophobic film was formed. In those cases the spectra indicate more orderliness, as shown in the traces for $m = 19$ and 18. A weak odd–even effect also can be distinguished. In the low frequecy region (Figure 9b), a strong and broad peak around 1544 cm^{-1} is assigned as the $\nu_a(CO_2^-)$. In conjunction with the peak at 1426 cm^{-1} (assigned as $\nu_s(CO_2^-)$), a tilted binding group is suggested. The contact angles θ_{HD}, θ_{BCH}, and θ_{H2O} all appear lower than the corresponding values observed for the monolayer formed on silver.

Discussion

We start by considering the monolayer structure formed on silver first. Compound I (as well as II) can be considered as composed of two parts: the aryl carboxyl group as the "effective head" group and the linear hydrocarbon tail group. The ellipsometry data shown in Figure 1 provide a nice qualitative support regarding the monolayer character and the proposition that the hydrocarbon tail group has the same tilt within each series of compounds (linear correlation with chain length) and that compound I has a "taller" head group than compound II, which in turn has a taller one than compound III (relative magnitude of intercepts). Difference in the slopes of the plots between various series was also noted. However, quantitative interpretation of the ellipsometry data in relation to head group orientation and chain tilt is tenuous because of the uncertainty in parameters such as index of refraction (we have been using $n = 1.47$ for all the films), surface morphology, physisorbed contamination (before acid adsorption), and corrosion and dissolution of the metal oxide surface, all of which may introduce error in the thickness calculation. Our information on the structure mainly comes from IR data. For the lower part of the monolayer structure of I on the silver surface, the carboxyl group must bind to the surface symmetrically with the biphenyl ring oriented perpendicularly to the surface. While there is no direct evidence as to the relative orientation of the biphenyl rings with respect to each other, the most efficient packing geometry would be that having the ring planes parallel to each other, considering

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(35) Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, 93, 767–773.

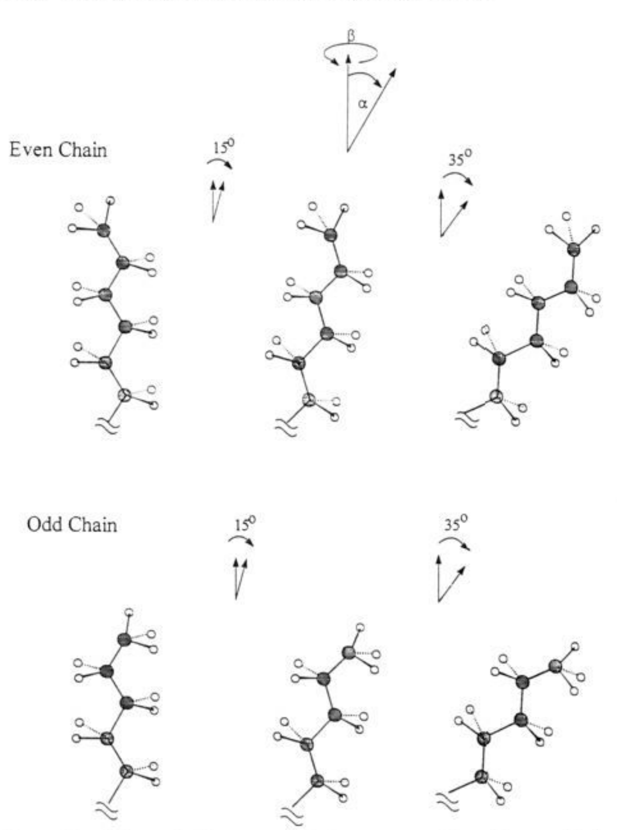

Figure 12. Schematic diagram of chain geometry of an all trans chain with respect to the surface.

the disk-like nature of the biphenyl moiety and larger tilt of the chain (see below). The total disappearance of the out-of-plane deformation band of the aromatic C-H's suggests the inclination of the ring faces toward the substrate surface (say, for better π–π stacking) should be small, if there is any at all. The hydrocarbon tail group connected to the biphenyl group through the C–O single bond constitutes the upper portion of the monolayer. The peak positions for the methylene vibration modes suggest a well-ordered and close-packed state of the chains. The presence of an odd–even effect in the methyl vibration modes and contact angle provides valuable information regarding the orientation. Such an effect was also observed in the SAMs of *n*-alkanoic acid on Ag and was used to draw the conclusion that the molecular chains are tilted. Closer analysis of the origin of the odd–even effect is instructive:

When considering an all trans polymethylene chain at a surface, the chain geometry with respect to the surface can be described by a cant angle, α, from the surface normal and a chain twist angle, β, along the chain axis as shown in Figure 12. For a normal orientation ($\alpha = 0$), the projections of the transition dipole for the vibration modes of the methyl group along the surface normal will also be identical for odd and even chains. A wetting liquid will sense identical surfaces whether it is odd chain or even chain. Thus no odd–even effect on the contact angle as well as the methyl vibration intensities is expected. However, as the chain starts to tilt in the positive direction (defined to be the direction to have symmetrically bound carboxylate group), the top surface also starts to differ between odd chain- and even chain-derivatized monolayers. Thus, for an even carbon chain, the terminal methyl group points closer to the surface normal, and the *z*-component of the transition dipole (and thus the IR intensity) associated with the symmetric stretch vibration mode for the methyl group ($\nu_s(CH_3)$) will increase with increasing chain tilt, to a maximum when the methyl groups oriented perpendicularly to the surface. Further tilt result in a decrease. The z-component of the transition dipole associated with the asymmetric mode ($\nu_a(CH_3)$), on the other hand, will decrease with increasing chain tilt, to a minimum (zero intensity) when the methyl group is oriented perpendicularly to the surface. Further tilt results in an increase. During the tilting action, the methylene unit next to the terminal methyl group is brought to the "interior" of the assembly (or moved away from the very monolayer/air interface). For an odd chain, the *z*-component of ($\nu_s(CH_3)$) will decrease with increasing chain tilt, to a minimum when the methyl group orientation is parallel to the surface. Further tilt results in an increase in the *z*-component. The asymmetric mode will vary in the opposite direction. During the tilting action, the methylene unit next to the terminal methyl group is brought "out" (or moved closer) to the very interface. The difference between odd- and even-chain system (in terms of terminal methyl group orientation and exposure or burial of the neighboring CH_2) is expected to increase with increasing tilt. Rotation along the molecular axis (increasing chain twist β) will, however, diminish the difference.[36] A 90° chain twist will totally smear out the difference brought about by any tilting angle. The twist action also results in a relative intensity change in the symmetric and assymetric methylene stretching modes $\nu_s(CH_2)$ and $\nu_a(CH_2)$, i.e. $\nu_s(CH_2)$ will decrease and $\nu_a(CH_2)$ increase with increasing twist. A detailed quantitative treatment of the variation in each mode in a reflection absorption has been described by Allara et al.[36] In addition, the tilting process in a monolayer assembly involves changes not only in the functional group orientation but also in the lattice spacing. Increasing space is needed for a larger tilt.

Figure 5 summarizes the odd–even effect on the intensity of methyl vibration modes for series **I** and **II** . Also included are the results for two other systems, *n*-alkanoic acids (**III**) on Ag and *n*-alkanethiols (**IV**) on Ag. It is seen that in the alkanethiol/Ag system, a very weak odd–even effect was observed.[37] The other three systems are all carboxylic acid derivatives. The magnitude of variation increases on going from **IV** to **III** to **I** and **II**. **I** and **II** have very similar variation amplitudes. Figure 6 summarizes the odd–even effect on contact angle. While there is no alternation within experimental error in the thiol/Ag system, a 5° difference was observed in θ_{HD} for odd- and even-chain *n*-alkanoic acid monolayers. The magnitude of odd–even alternation is even larger, up to a 10° difference between odd- and even-chain derivatized biphenylcarboxylic acid and naphthoic acid monolayers. Examination of Figures 4 and 5 reveals a correlation of odd–even effect in contact angle and intensity of methyl vibration; i.e., *the higher the odd–even alternation in the methyl vibration mode's intensity, the higher the odd–even alternation in contact angle.*

The increasing odd–even effect observed is believed to be due to an increasing difference in the terminal methyl orientation in odd-chain and even-chain systems, brought about by the increasing chain tilt. This conclusion is also supported by the increasing intensity of methylene stretches (both symmetric and asymmetric modes) in going through the same series (Figure 4). The chances of having the same chain tilt but different chain twist (lower chain twist for **I** and **II**) is ruled out by an analysis of the relative intensities of $\nu_s(CH_2)$ and $\nu_a(CH_2)$. (That is, $\nu_a(CH_2)$ does not decrease in going from **III** to **I** and **II**). That the contact angle on odd-chain systems is lower than the angle on even-chain systems can be attributed to more exposure of the methylene group in the former case. With even-chain derivatives, the contact angle also increases with tilting (i.e. 47° to 50° to 54° and 53° in going from

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[36] Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927–945.

[37] The magnitude of variation is small but real, after numerous careful measurements. However, close examination of the trend indicated differences between thiol/Ag and carboxylic acid/Ag (and the trend in the *n*-alkanethiol/Au system as well[8]): The symmetric stretching mode is lower for odd chain and higher for even chain. This is just the opposite to the case of the carboxylic acid system. This has to do with the tilt direction. While acid derivatives and thiol on Au tilt in the positive direction, thiol on Ag tilts in the negative direction. See the Raman study of the orientation of the C–S bond in thiol/Au and thiol/Ag: Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284–8293.

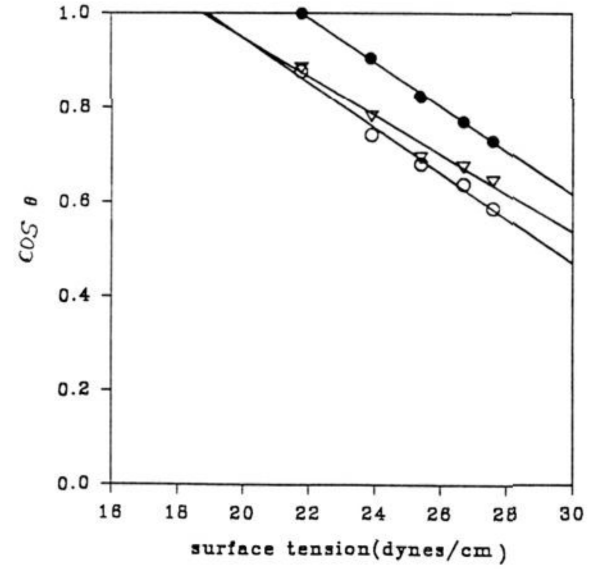

Figure 13. Critical surface tention γ_c of a monolayer of **I** on Ag: ○, **I** with $m = 15$; ●, **I** with $m = 16$; ▽, Teflon surface.

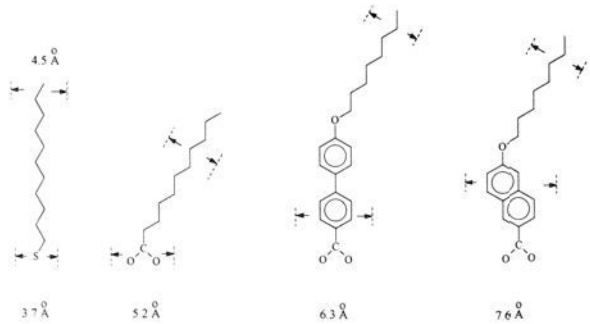

Figure 14. van der Waals diameters of the monolayer-forming amphiphiles.

IV to **III** to **I** and **II**), presumably because of less and less exposure of the next methylene unit from the surface. With odd-chain systems, the contact angle decreases with increasing chain tilt (47°, 45°, 43°, and 43° in going through the same series), presumably because of more and more exposure of the next methylene unit. This agrees with the suggestion that the hexadecane contact angle is of very short-range interaction and is sensitive to the very top ~2 Å from the surface.[38] The critical surface tensions of wetting, γ_c, on a monolayer of **I** with even-chain and odd-chain tail groups were measured with a homologous hydrocarbon as wetting liquid (Figure 13). The even-chain derivative gave 19 dyn/cm, which is 3 dyn/cm lower than that for the odd-chain analog and is similar to that measured on a Teflon surface. Only hydrocarbon liquid is sensitive to the orientation of the terminal methyl group presumably because the dispersive component is dominant in the interfacial interaction where the polar component is important in the surface tension of water. (Alternatively, the smaller water molecules can penetrate farther down; thus they do not sense much difference in the orientation change occurring in the top 2-Å region.[39])

Then what is the cause of increasing chain tilt? Figure 14 shows the "effective" size of the head group in each system, as estimated from molecular shapes and van der Waal diameters. The hydrocarbon chain is attached to the surface through the reactive head group, and the interchain spacing is determined by the lattice spacing of the head group, which in turn is determined by the head group/substrate interaction as well as the "size" of the head group. Thiol on Ag represents a system where the size of the head group does not play a role because it is smaller than the other size constraint, i.e. the cross section of the polymethylene chain. The experimental observation that this system has the densest packing of the chains that is allowed by the van der Waals diameter of the chain and exhibits little tilt from the surface normal could mean the dominant role of interchain interaction causes reorganization of the overlayer lattice (or adopting whatever sites) to achieve a closest packing. On the other hand, *n*-alkanoic acid on Ag represents a system where the size of the head group cannot be ignored, as it is larger than the cross section of the polymethylene chain. In light of the surface X-ray diffraction result,[19] showing that *n*-alkanoic acid molecules adsorbed on specific sites on Ag(111) and forming a *p*(2x2) overlayer with a lattice spacing of 5.78 Å, the picture of the binding lattice for *n*-alkanoic acid can be depicted as in Figure 15. A symmetrically bound head group which requires at least 5.2 Å of space can be accommodated in the proposed lattice. Such an arrangement inevitably results in free volume between the molecular chains. The hydrocarbon chain is thus tilted toward the nearest neighbor to maximize van der Waals contact. For compounds **I** and **II**, the head group size is increasingly large, i.e. a 6.4 Å × 3.4 Å moiety in **I** (the dihedral angle between the two phenyl rings is known to be small in the solid state[40]) or a 7.6 Å × 3.4 Å moiety in **II** needs to be accommodated in the monolayer packing. More space is expected to be created between tail chains

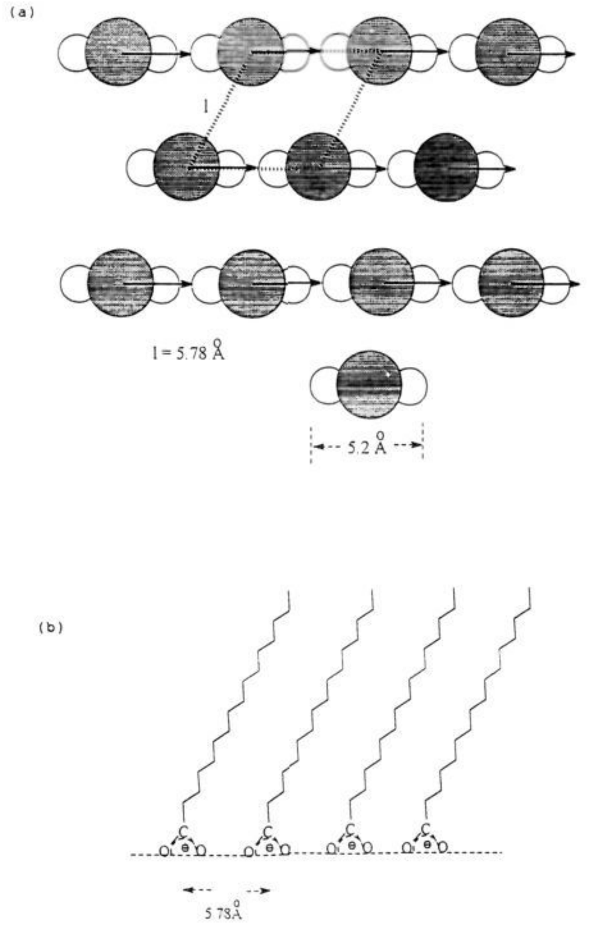

Figure 15. Binding lattice of an *n*-alkanoic acid monolayer on Ag. (a) Top view. The filled circles represent the carbon atom of the carboxylate; the smaller open circles represents oxygen atoms. The arrow points to the direction of the chain tilt. (b) Side view along the edge of a unit cell.

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(38) Bains, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506–512.

(39) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897–5898.

(40) (a) Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1977**, *83*, 1586. (b) Troter, J. *Acta Crystallogr.* **1961**, *14*, 1135.

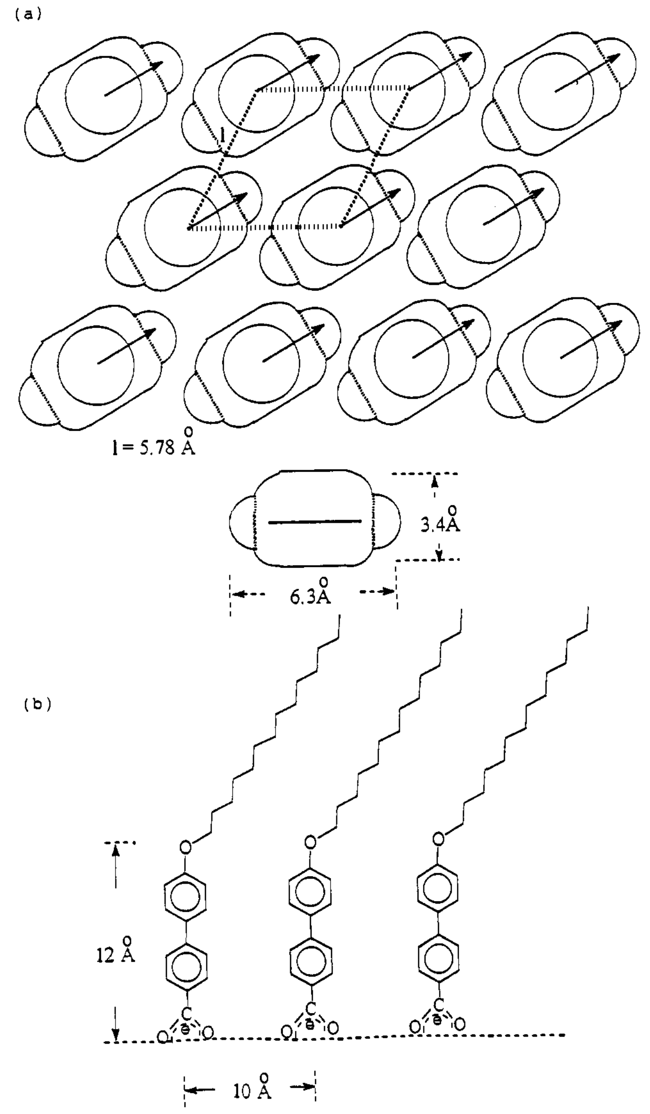

Figure 16. Proposed structure of a monolayer of I on Ag: (a) top view of the van der Waals contour of the biphenyl group; (b) side view along the diagonal line of a unit cell.

in going from **III** to **I** to **II**. However, it was noted that the odd–even effect in IR intensities and contact angle is very much similar for the latter two systems, which may imply a similar chain tilt even though the steric requirement is quite different. This outcome can be possible if the binding sites are specific and both compounds are occupying the same lattice structure. The most plausible picture is the following. Both **I** and **II** are adopting the same lattice as *n*-alkanoic acid does on silver for maximum packing as well as site specificity reasons. The dilema of the same packing lattice of the head group but different chain tilt (between **III** and **I**, **II**) can be reconciled by considering the orientation of the aromatic plane. Considering the disk-like nature of the aromatic chromophore, the only way to arrange the head groups in such a lattice spacing without confronting each other would be as shown in Figures 16 and 17. In the top view of Figure 16a, the van der Waals contour of the biphenyl moiety is drawn at the distance of the proposed lattice (5.78 Å). The plane of the ring is lined up toward the second nearest neighbor (diagonal direction of the unit cell). It can be seen that compound **I** can comfortably fit in the same lattice adopted by *n*-alkanoic acid. The "side view" of Figure 16b shows that the neighboring molecules along the diagonal line are at a distance of 10 Å. In Figure 17, it is shown that the naphthyl groups are in tight contact with nearest neighbors. The steric requirement of a naphthoic group may be reduced by a slight tilt of the head group. The

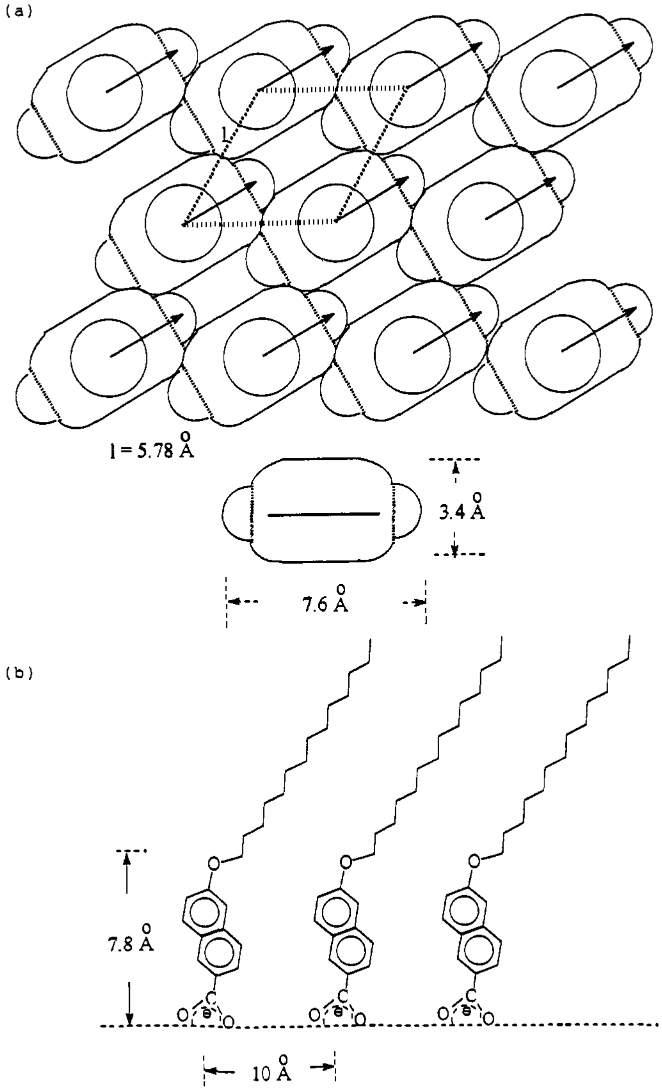

Figure 17. Proposed structure of a monolayer of **II** on Ag. Same meaning as in Figure 16.

broad band around 1485 cm^{-1} in the spectrum of a monolayer of **II** might indicate such tilting (i.e. showing up of $\nu_a(CO_2^-)$ at the expense of $\nu_s(CO_2^-)$). The explanation for the observation that the hydrocarbon tail is more tilted than the *n*-alkanoic acid system while adopting the same binding lattice is that the chain is *not* tilting toward the nearest neighbor as in the case of *n*-alkanoic acid. The most favorable conformation for the ether C–O–C linkage would have the $O–C_{alkyl}$ bond eclipsing the ring plane.[41] This constraint would induce the chain to tilt toward the *second nearest* neighbor, in a direction of more empty space. Such a tilting direction was believed to be the cause of high tilt in *n*-alkanethiol on the GaAs(100) surface.[9] For *n*-alkanoic acid on Ag, this tilting option is also available, but there will be more energy gain by adopting minimum tilt if other things are equal.[20]

An alternative proposal is that, for compound **I**, the effective head group is larger than the lattice spacing of 5.78 Å adopted by *n*-alkanoic acid. The spacing between nearest neighboring head groups is forced to increase. Thus an expanded lattice was adopted by the molecules. This would mean lower coverage of the surface. The alkyl tail groups necessarily tilt more (toward the nearest neighbor) in order to maximize the van der Waal contact in forming a closely packed monolayer. Compound **II** adopts the same binding sites as **I**, giving the same chain tilt. Some tilting of the head group for **II** is needed to fit into the

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(41) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; p 107.

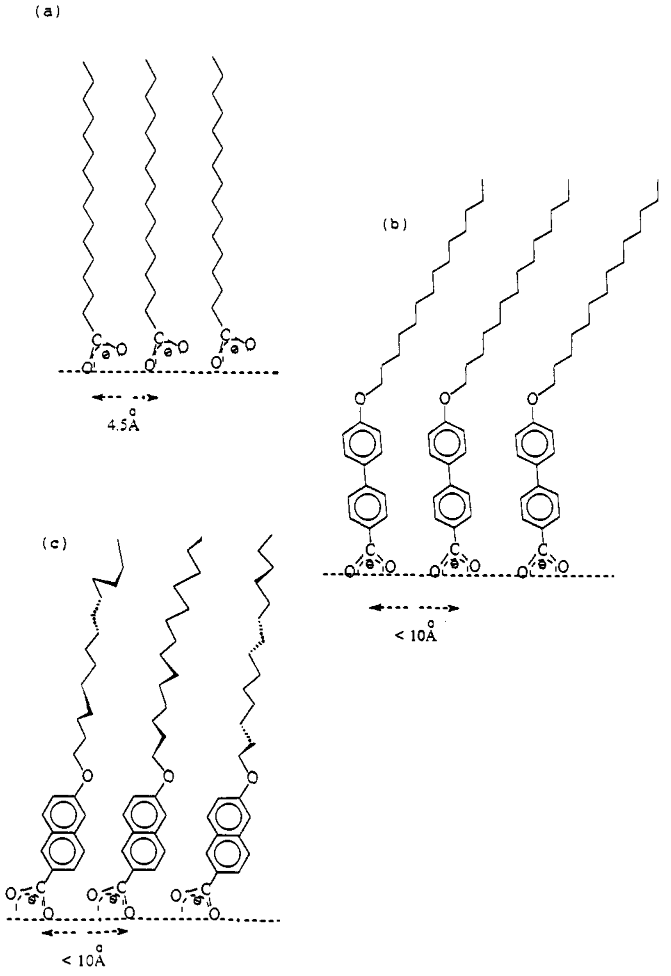

Figure 18. Proposed structure of a monolayer. Side view of (a) III on Cu, (b) I on Cu, and (c) II on Cu.

lattice. The current data can not differentiate the two alternatives, while diffraction or STM measurement would.

As for the copper surface, earlier study under ultra-high-vacuum (UHV) conditions has shown that a carboxylic acid can adopt either symmetric binding or cant binding depending on the surface coverage.[42] This implies the binding sites on copper may not be specific and the binding geometry of carboxylate does not have to be in a certain configuration. (In contrast, only symmetric binding was ever reported for carboxylic acid derivatives on Ag.[34,43,44]) *n*-Alkanoic acid on Cu represents a case where interchain interaction dominates so that a normal orientation is adopted. A simple geometry analysis shows that a tilt of 34° of the symmetrically bound carboxylate group would reduce the space requirement from 5.2 to 4.5 Å, a value comparable to the van der Waals diameter of the polymethylene chain! And 34° is what it takes to have a normal orientation (Figure 18a). This is how the carboxyl head group can be accommodated in a densest packing that is determined by the van der Waal diameter of the polymethylene chain. In the case of compound **I**, a well ordered monolayer film can also be formed on the copper surface. The hydrocarbon tail groups are tilted, as evidenced by the odd–even effect in both IR intensity and contact angle, but to a lesser extent than on the silver system. There is an uncompromisable and dominant size constraint in **I**, the biphenyl group. Some evidence of tilted binding geometry albeit much less tilted than the binding geometry of *n*-alkanoic acid was indicated by IR. This is not surprising as high tilt of the biphenylcarboxyl group demands more space between the head groups. It is proposed that compound **I** packs as close as possible on Cu, only limited by the size of the biphenyl chromophore. The binding lattice is smaller than the binding lattice on Ag because sites are specific (as well as stronger) for the latter. Chain tilt is smaller because of the reduced lattice spacing. For compound **II**, the binding geometry of the naphthoic group is clearly tilted. As shown in Figure 18c, significant tilt of the head group can reduce the space requirement of the head group for a higher packing. But poor matching (or incommensurability) of the head group lattice and the lattice of ordered chain assembly precludes the formation of an ordered film. The chains are less ordered, as evidenced both from IR and contact angle measurement.

Conclusion

We have demonstrated here that a biphenyl group or naphthyl group causes higher tilt of molecular chains in carboxylic acid monolayers on silver and a correlation of wetting property and chain tilt. (Similar results were also found with just one phenyl group incoporated in the chain.) The higher chain tilt is proposed to result from different tilting direction of the molecualr chain within the same binding lattice (or the same tilt direction in an expanded binding lattice). Different behavior observed on silver and copper has to do with site specificity, binding geometry, and binding strength, among other things. Similar consideration might be applied to understand the difference between thiol/Au and thiol/Ag systems.[45] In conclusion, the ultimate structure of a monolayer assembly is a balance of various interactions and requirements, including head group/substrate interaction, chain–chain interaction, lattice spacing, and size limitations. All these factors should be considered in designing more complex systems.

Acknowledgment. Financial support from the National Science Council, Republic of China, is gratefully acknowledged.

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(43) Schlotter, N. E.; Porter, M. D.; Bright, T. B.; Allara, D. L. *Chem. Phys. Lett.* **1986**, *132*, 93–98.

(44) Chau, L. K.; Porter, M. D. *Chem. Phys. Lett.* **1990**, *167*, 198–204.

(45) The thiol analogs on Au gave similar results in terms of IR and wetting properties. Results to be published.