Rigid-Rod Langmuir–Blodgett Films from [n]Staffane-3-carboxylates

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The rigid-rod surfactants [n]staffane-3-carboxylates (1[n]) readily form Langmuir–Blodgett films when n = 4 and, with some effort, also when n = 3. The area per molecule, extrapolated to zero pressure, is nearly independent of the counterion (25.0 Å²/molecule). Bilayer thickness in a multilayer assembly is 25.8 ± 0.1 Å for Ca²⁺ 1[3], 32.2 ± 0.1 Å for Ca²⁺ 1[4], and 31.4 ± 0.1 Å for Cd²⁺ as determined by low-angle X-ray reflection. Ellipsometry yields the bilayer thickness 25.7 ± 0.1, 32.3 ± 0.1, and 32.6 ± 1.0 Å, respectively. The average tilt angle deduced from the difference between 1[3] and 1[4] is 17 ± 5°. Independent IR measurements at normal incidence on Ge and grazing angle incidence on Au substrate yield the values 28 ± 2° and 19 ± 2°, respectively. Only IR measurements were possible for a monolayer. They yielded the value 27 ± 2° at normal incidence on Ge and a distinctly different result at grazing incidence on Au, 0–10°. The larger average tilt values on the Ge surface are attributed to surface roughness.

The recent surge of interest in Langmuir–Blodgett (L-B) multilayer structures has been driven at least in part by the promise that these materials hold for supramolecular engineering in areas such as nonlinear optics, pyroelectrics, and electron transfer studies. The salts of fatty acids, the usual construction materials for the films, are less than ideal for many of these applications. This is due at least in part to the floppy nature of the aliphatic chain, and it would be useful to find alternative L-B materials that have the form of rigid rods.

We have recently published the synthesis of [n]staffane-3-carboxylic acids 1[n], linear rigid-rod analogs of fatty acids. We now report that these materials form Langmuir–Blodgett films readily and provide an initial characterization of their structure.

Experimental Part

Samples. The preparation and purification of 1[3] and 1[4] have been reported.

Area–Pressure Isotherms. Standard procedures were followed, using a Model P Lauda preparative film balance (Brinkman Instruments). The acid 1[3] was introduced in chloroform solution (1 g/L), and 1[4] in a 4:1 chloroform–acetonitrile mixture (0.5 g/L). Before compression, the solvent was allowed to evaporate for 15 min. A base line was checked to make sure that no excess solvent remained. Counterion effects were investigated by adding inorganic salts to the aqueous subphase to yield cation concentrations of 5 × 10⁻⁴ M. A 0.5 M NaOH solution was added to adjust the pH to 7.0 ± 0.3 (i.e., the subphase solutions were unbuffered). Measurements on 1[3] were only possible when its solubility was decreased by saturating the aqueous layer with CaCl₂ (pH = 8.3). The isotherm of cadmium arachidate was measured as a standard.

Film Transfer. The films were transferred to a flat solid substrate by withdrawal or immersion under a constant pressure of 25 mN/m at a subphase temperature of 22.0 ± 0.5 °C. Silicon wafers polished on one side [N(100), Aurel Co.] served as substrates for ellipsometry (50 × 8 × 0.2 mm) and low-angle X-ray reflection (30 × 15 × 0.2 mm). They were ultrasonicated in chloroform twice for 10 min and treated with a very dilute solution of octadecyltrichlorosilane in chloroform to create a hydrophobic surface. Germanium (30 × 15 × 2 mm) was used as a solid substrate for normal incidence IR transmission measurements (Wilmad Glass Co.). It was cleaned by dipping into chromic acid for a few seconds and rinsed with a copious amount of water. Glass microscope slides (40 × 25 × 1 mm) with a 1500-Å layer of sputtered gold were used as substrates for grazing incidence IR reflection measurements. Just before film deposition, the IR substrates were briefly rinsed with a chromic acid solution and then washed with an excess of Millipore water (18 MΩ) to produce a hydrophilic surface. Y-type deposition was observed on all of the substrates; i.e., layers were deposited on both the dipping and the withdrawing stroke. The transfer ratio was 0.92–1.10.

Measurements. Ellipsometric measurements were performed using a Rudolph Model 437 ellipsometer (Rudolph Research, Flander, NJ) equipped with a Model RR2000 automatic rotating analyzer and interfaced to a Hewlett-Packard Model 915B desktop computer. Several strips of 2n layers (n = 0–6) were deposited next to each other on a single silicon substrate. Measurements were performed at 632.8 nm (He–Ne laser) and at an incidence angle of 70°. Data were expressed in terms of the conventional ellipsometric parameters as Δ = Δ° − Δ and Ψ = Ψ° − Ψ, where Δ° and Ψ° refer to the bare substrate.

Low-angle X-ray reflection patterns of the L-B films were obtained on an assembly of seven bilayers using an automated Model APO 3620 Phillips powder diffractometer fitted with a
dissolved beam graphite monochromator and a theta compensating slit (Cu Kα = 1.54178 Å). This arrangement permitted diffraction lines to be measured down to about 2θ = 1°, with a precision of about ±0.02°. The program written for data analysis directly calculates the electron density distribution of the multilayer systems following the basic method of Hosemann and Bagchi12 to obtain the total Patterson function and the deconvolution method of Pape13 to obtain the Patterson function of one unit cell.

Infrared measurements were performed on a Nicolet Model 60SX Fourier transform instrument with a HgCdTe detector cooled with liquid nitrogen and a wire grid polarizer (IGP225, Cambridge Physical Science), using 2000 scans and a resolution of 0.5 cm\(^{-1}\). A Harrick Model RMA-00G reflection attachment was used for reflection measurements, using an incidence angle of 84°. Isotropic spectra were measured in a KBr pellet.

Results and Discussion

Our initial objective was to find out which, if any, \([n]\)-staffane-3-carboxylic acids (\([1n]\)) and salts form L-B films. We found that the first three acids (n = 1–3) are too soluble in water to form such films. However, \([13]\) will form a film on a concentrated aqueous solution of CaCl\(_2\), and this film has been transferred successfully to various solid substrates. The fourth member of the series, \([14]\), has optimal properties and forms films readily on pure water, and these transfer well. No deterioration with time was observed. The fifth acid, \([15]\), was found to be too insoluble in all organic spreading solvents tested, and we have not been able to use the standard techniques to make an L-B film of it.

Once it was established that \([14]\), and to a lesser degree, \([13]\), are suitable for the formation of L-B films, we became interested in characterizing their internal structure. While a thorough characterization of a two-dimensional structure requires a fair investment of effort, an initial survey of film thickness and determination of the rod tilt angle can be performed relatively simply. We have used ellipsometry, low-angle X-ray reflection, and IR spectroscopy for this purpose. While the first two methods are absolute, the sensitivity offered by the instrumentation accessible to us is such that only multilayers can be investigated. IR spectroscopy requires independent knowledge of IR transition moment directions in \([1n]\), which we have obtained in a separate investigation,14 and the FTIR spectrometer available to us had sufficient sensitivity to record reliable spectra even for a monolayer. The results revealed an interesting difference in the packing of a monolayer and a multilayer, and a future detailed two-dimensional structural investigation appears warranted.

Isotherms. The films were characterized by pressure–area isotherms. These were measured for \([4]\) with a series of counterions (Figure 1) and for \([13]\) with Ca\(^{2+}\) counterion (Figure 2). The course of all of the isotherms is very similar and consists of a gently rising part ("two-dimensional liquid") and a steeply rising part ("two-dimensional solid"). The near identity of the curves for \([13]\) and \([4]\) strongly suggests that these molecules pack in the same manner.

The "liquid" part of the isotherm is far more pronounced for \([1n]\) than it is for the standard L-B material, cadmium arachidate, shown in Figure 2 for comparison. Linear extrapolation of the steeply rising part to zero pressure yields exactly the same limiting area for \([13]\) and \([4]\), 26.0 Å\(^2\)/molecule, essentially independent of the nature of the counterion. Film collapse occurs at about 45 mN/m for \([13]\) and 50 mN/m for \([4]\), at 24.5 Å\(^2\)/molecule.

The "zero-pressure" extrapolated area per molecule, 26.0 Å\(^2\)/molecule, and the area of molecule at the point of collapse, 24.5 Å\(^2\)/molecule, are both significantly larger than the corresponding numbers that we obtain for cadmium arachidate, 20 (reported15 19–21 Å\(^2\)/molecule) and 18 Å\(^2\)/molecule, respectively. This result is compatible with the bulkier shape of the cylindrical \([n]\)-staffane rod compared with an n-alkane chain, known from the simple crystal X-ray structures of the parent hydrocarbons, \([3]\)-staffane and \([4]\)-staffane,16 and of many derivatives.17 The packing in the single crystals of the hydrocarbons is of the herring-bone type, with the molecular axes tilted at 21° (\([3]\)-staffane) or 20° (\([4]\)-staffane) from the crystal axis. The \([n]\)-staffane rods mesh so that the bulging cages of one rod snuggle against the narrower waists between the cages on a neighboring rod. The repeat distance between the cages within a rod is 3.34 Å, and the separation of the parallel axes on the closest neighbors is 5.36 Å.

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If the \([n]\)staffane cores of the molecules in our film were perpendicular to the water surface, such meshing would result in a radius of only 2.68 Å. Half of the molecules would have to be 1.67 Å further from the surface than the other half, but the projection of each molecule on the water surface would be close to a circle merely 22.6 Å² in area. The actual surface area per molecule in the compressed film would then depend on the nature of the two-dimensional packing. For instance, in a square lattice, which permits perfect neighbor meshing, it would be 28.8 Å².

Some meshing clearly occurs, since in its absence, with all molecules equidistant from the surface, the perpendicular orientation would cause each molecule to project a near circle with an area of 32.7 Å² as estimated using standard van der Waals radii. This is significantly in excess of the measured value. However, the meshing can be achieved by keeping the molecules equidistant from the surface and tilting them ~20° from the normal, as they are in the hydrocarbon crystal. This yields an area of 28.2 Å²/molecule.

While the measured area per molecule alone clearly will not permit us to deduce the molecular packing arrangement, its magnitude lies comfortably within reach of the above packing schemes and others that can be readily envisaged.

Additional information on the packing can be obtained from independent knowledge of the tilt angle. We have sought to determine this in two ways: (i) from the knowledge of the change of the metal ion to metal ion repeat distance upon going from \(1[3]\) to \(1[4]\), i.e., extending the length of the staffane rod pair by 6.68 Å; (ii) from band intensities in IR spectra.

**Ellipsometry.** A plot of \(-\Delta\) against longitudinal position of a sample covered with a series of strips revealed a regular series of steps corresponding to the increasing number of layer pairs deposited. The data points in the plateau regions were averaged. The fit of the \(\delta \psi\) versus \(\delta \Delta\) growth curve to theory was best when the refractive index of the film was assumed to be \(n_r = 1.65 \pm 0.001\). The standard value, \(n_r = 3.84 - 0.12i\), was used for the silicon substrate. The value of \(n_r\) is higher than the usual \(n_r \approx 1.50\) for fatty acids, but this is in line with the higher density of \([n]\)staffane derivatives.\(^{18,17}\)

A linear plot resulted for film thickness versus the number of layers (Figure 3). Results for average thickness of a pair of layers derived from these measurements are 27.2 ± 1.0 Å for \(Ca^{2+} 1[3]\), 33.2 ± 1.0 Å for \(Ca^{2+} 1[4]\), and 32.6 ± 1.0 Å for \(Cd^{2+} 1[4]\). Much of the ±1.0 Å uncertainty in the results originates in factors such as the assumed refractive index and affects results for \(1[3]\) and \(1[4]\) in the same direction. We estimate their difference to be 6.0 ± 0.8 Å, somewhat less than the 6.68 Å expected in the absence of tilt. If the packing of \(1[3]\) and \(1[4]\) is indeed the same, this yields an average tilt angle of 13°–35° for the \(Ca^{2+}\) films.

**Low-Angle X-ray Reflection.** Figure 4 shows low-angle X-ray reflection intensity recorded for the assemblies of seven bilayers of LB films of \(Ca^{2+} 1[n]\), \(n = 3\) and 4. The film exhibits high order. Literature procedures\(^{18}\) were used to correct the peak intensities for all specimens for a \(\sin \theta\) intensity variation due to the theta-compensating slit system and for polarization effects.\(^{19}\) Peak separations yield repeat distances between \(Ca^{2+}\) ion layers as 25.8 ± 0.1 Å and 32.2 ± 0.1 Å for \(1[3]\) and \(1[4]\), respectively, i.e., an increase by 6.4 ± 0.14 Å upon a 6.68-Å increase in the length of a rod pair. This yields an average tilt angle of 12°–21°.

Analysis of peak intensities yields the electron density distribution in the unit cell of the \(Ca^{2+}\) \(1[3]\) and \(1[4]\) multilayers (Figure 5). The electron density curves are subject to the usual\(^{18}\) truncation artifact which appears as a deep second well after the metal cation peak at the graph edge, and they have a finite resolution of only 1.5 Å. Both of these limitations are dictated by the finite number of observed Bragg reflections.

Within these constraints, it is still possible to interpret three features of the density graph: (i) the high electron density associated with the \(Ca^{2+}\) ion at the top and the bottom of the unit cell; (ii) the very low electron density associated with the plane of van der Waals H–H contacts in the center of the unit cell; (iii) an intermediate region of oscillating electron density. The peaks located in this region are presumed to correspond to the methylene carbons of the bicyclo[1.1.1]pentane cages in the staffane, and the troughs to the intercage C–C bonds. Although the available resolution does not permit us to use the observed separations between peaks to determine the packing geometry, its size clearly is of the right order of magnitude, about 3–3.5 Å. The amplitude of the oscillations is determined by the intensities of the Bragg peaks of orders 8, 9, and 9–11 in the case of \(1[3]\) and \(1[4]\), respectively. The lower amplitudes observed for \(1[3]\) indicate a lower degree of ordering in this multilayer, and this is probably associated with the presence of a saturated \(CaCl_2\) solution during the deposition process. The failure of the electron density to drop to values as low as observed

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\(^{18}\) Leszlauer, W.; Blasius, J. K. Biophys. J. 1972, 12, 175.

\(^{19}\) Blaurock, A. E.; Worthington, C. R. Biophys. J. 1966, 6, 305.
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In contrast, the carboxylate-carrying terminal cages lying
across the ionic contact plane are rather close to each other:
6.4 Å in 1[3] and 5.8 Å in 1[4]. It is hard to say
just what distance to expect from the covalent and ionic
radii in the absence of detailed packing information, but
it is clear that the anions and cations are meshed and
nearly in the same plane, as proposed for manganese stearate.20

For 1[4], the measurement was repeated with Cd2+ as
the counterion (Figure 6). The Cd2+-Cd2+ layer separation
was 31.4 ± 0.1 Å. Up to 17 reflection peaks were observed
in this case, and these films appeared to be of superior
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Figure 5. Projection of the relative unit cell electron densities
in L-B films of Ca-[n]staffane-3-carboxylates, (a) n = 3 and (b)
n = 4, onto the surface normal. The vertical scale is arbitrary.

Figure 6. Low-angle X-ray reflection of Cd-[4]staffane-3-
carboxylate. The substrate background has been subtracted.

Figure 7. Projection of the unit cell electron densities onto the
surface normal for Cd-[4]staffane-3-carboxylate.

of the film thickness by the less accurate ellipsometric
method may be due to an error in the n values assumed. The
effect of such an error on the determination of the tilt
angle would be small, because of its differential nature.

Accepting the X-ray values as the more accurate, and
accepting a tilt of 17 ± 5°, we can derive the effective
length of a back-to-back arranged rod pair. This is 27.0
Å for Ca2+ 1[3], 32.8 Å for Ca2+ 1[4], and 32.8 Å for Cd2+
1[4]. These values are quite reasonable and support our
analysis, including the critically important assumption

Admittedly, the values to be expected are not very well
defined in the absence of information on the details of the
packing. If the rods in the two bilayers were antiparallel
and coaxial, with the metal ion on the axis, one would
expect an end-to-end length of about 37 Å for 1[4] salts
from the single-crystal X-ray analysis of 1[2]17 and of the
parent [n]staffanes,16 standard van der Waals radii for
hydrogen, and ionic radii for Ca2+ or Cd2+. The observed
value of 33--34 Å again suggests that interdigitation occurs
at the interlayer contact planes.

The small difference between Ca2+ 1[4] and Cd2+ 1[4],
apparent in both methods of measurement, seems to be
real and may be due to differences in packing of the metal
ions.

We next present the results of IR measurements on the
multilayer assemblies, which provide an independent
estimate of the tilt angle and its dependence on the nature
of the counterion. Since they had to be performed on
different substrates, the molecular orientation in the first
layer could be different, but this would not be likely to affect significantly the average value for the multilayer assembly.

**IR Spectroscopy. General.** A prerequisite for the use of IR spectroscopy for the characterization of L-B multilayers and monolayers is the knowledge of transition moment directions of the prominent vibrations in the individual constituent molecules. The IR transitions in the (n)staffane skeleton (21,22) as well as those in the carboxylate group are well understood. In the absence of perturbations by the counterions, transitions in the salts of [1(n)] fall into four classes: (a) nondegenerate transitions polarized along the 3-fold symmetry axis of the (n)staffane framework, such as the terminal CH stretch at about 2980 cm\(^{-1}\), the CH\(_2\) wag near 1215 cm\(^{-1}\), and the symmetric CO\(_2\) stretch near 1440 cm\(^{-1}\); (b) nondegenerate transitions polarized along the \(000\) direction of the CO\(_2\) group such as the antisymmetric CO stretch near 1535 cm\(^{-1}\); (c) nondegenerate transitions polarized perpendicular to the plane of the CO\(_2\) group, which we have not observed; (d) doubly degenerate transitions perpendicular to the long molecular axis, such as CH\(_2\) stretches near 2870 and 2905 cm\(^{-1}\) (the degeneracy is exact in the parent hydrocarbons and should be removed to a small degree in the presence of the carboxylate group at one of the termini, but this splitting is unobservably small). The only other IR peak in our spectra that is sufficiently intense to be easily measurable is located at 2970 cm\(^{-1}\). It is to be of use for the present purposes.

**IR Intensities and Orientation Factors.** As long as the substrates are optically inert, the samples optically uniaxial, and the IR transitions well separated in the spectra, a quantitative evaluation of the results is straightforward.\(^{25}\) These conditions are well fulfilled for the normal incidence measurements on Ge substrates, but the metal substrate used in the grazing angle reflectance measurements complicates matters.\(^{25-26}\) Since we observe no peak shifts and no enhanced reflections, we shall assume that the simple treatment is adequate to the first approximation even in this instance, i.e., that the effect of the metal surface is merely to suppress all absorption that would be due to that component of a transition moment that is parallel to the surface.

We use the electric dipole approximation and assume that the changes of sample polarizability and refractive index with wavelength are the same in the film and in the isotropic powder. We introduce the usual definition of the orientation factor of the transition moment of the \(k\)th degenerate component of an \(n\)-fold degenerate \(i\)th vibration

\[
K_{ik} = \langle \cos^2 (\alpha) \rangle
\]

(1)

The pointed brackets indicate ensemble averaging and \((\alpha)\) is the angle between the transition moment of the \(k\)th component of \(i\)th vibration and the normal to the surface, \(Z\).

We label the peak intensities of transition \(i\) measured in the L-B film at normal incidence \(A_i\), those measured at grazing incidence \(A_i^G\), and those measured in the isotropic powder, \(A_i^{iso}\). Then, transitions \(i\) and \(j\) can be characterized by the ratios \(Q_{ij}^N\) and \(Q_{ij}^G\)

\[
Q_{ij}^N = \frac{A_i^{iso} A_j^N/A_j^{iso} A_i^N}{(n/m) \sum_k (1-K_{jk}) \sum_l (1-K_{jl})}
\]

(2)

\[
Q_{ij}^G = \frac{A_i^{iso} A_j^G/A_j^{iso} A_i^G}{(n/m) \sum_k K_{jk} \sum_l K_{jl}}
\]

(3)

We shall use the doubly degenerate CH\(_2\) stretching vibration at 2905 cm\(^{-1}\), which is of class \(d\), as our reference vibration \(j\), so that \(m = 2\). The measured ratios will then be labeled \(Q_{d}^N\) and \(Q_{d}^G\).

Using \(\alpha\) for the inclination of the (n)staffane axis from the surface normal \(Z\) and defining the average inclination \(\langle \alpha \rangle\) by \(\cos^2 (\alpha) = \langle \cos^2 (\alpha) \rangle\), we obtain

\[
\sum_k (1-K_{jk}) = 1 + \cos^2 (\alpha)
\]

(4)

\[
\sum_k K_{jk} = \sin^2 (\alpha)
\]

(5)

for this vibration and all other vibrations of class \(d\). For these vibrations, we therefore expect \(Q_{d}^N = Q_{d}^G = 1\), and measurements on more than one of them merely provide a consistency check.

For vibrations of the other three classes, which are not degenerate, \(n = 1\), and the subscript \(k\) is not needed

\[
Q_{d}^N = (1 + \cos^2 (\alpha))/2(1 - K_i)
\]

(6)

\[
Q_{d}^G = \sin^2 (\alpha)/2K_i
\]

(7)

Now, \(Q_{d}^N\) and \(Q_{d}^G\) contain information on the average inclination angle \(\langle \alpha \rangle\). The three classes of vibration differ in their values of \(K_i\), which describe the average orientation of their transition moments relative to the surface normal.

For vibrations of class \(a\)

\[
K_i = \cos^2 (\alpha)
\]

(8)

while for vibrations of classes \(b\) and \(c\), \(K_i\) reflects the orientation of the CO\(_2\) group relative to the surface. If the \(O-O\) direction lies in the surface, we have \(K_i = K_o = 0\) for a vibration of class \(b\), polarized along \(O-O\). Rotation of the OCO plane about the molecular long axis from this position by angle \(\beta\) yields

\[
K_i = K_o = \sin^2 (\alpha) \sin^2 (\beta)
\]

(9)

where \(\sin^2 (\beta) = \langle \sin^2 (\beta) \rangle\). When the OCO plane is perpendicular to the surface, \(K_i = K_o = \sin^2 (\alpha)\).

For a vibration of class \(c\), \(\sin^2 (\beta)\) would need to be replaced by \(\cos^2 (\beta)\) in eq 9 for \(K_i = K_o\), so that the results for \(O-O\) parallel to the surface and OCO perpendicular to the surface would be interchanged. However, we observe no vibrations of this class in our spectra.

Note that the statements about the \(K_i\) values for the transition moment directions hold only if the vibrations are those of the isolated molecule and are not affected significantly by the counterions. This is far more likely to hold for the 1215-cm\(^{-1}\) CH\(_2\) (class \(a\)) than the 1440-cm\(^{-1}\) symmetric CO\(_2\) stretch (class \(a\)) and the 1555-cm\(^{-1}\) asymmetric CO\(_2\) stretch (class \(b\)). We shall, therefore, use the \(Q_{d}^N\) and \(Q_{d}^G\) values obtained from the intensity of the 1215-cm\(^{-1}\) vibration as our primary tool for the evaluation of the average tilt angle \(\langle \alpha \rangle\). Substituting \(K_o = K_o = \cos^2 (\alpha)\) into eq 6 and 7, we obtain
angle counterion, and one could then obtain the average rotation expressions of the carboxylate multilayer of the 1440-cm⁻¹ CO₂-vibration agreed with that obtained from the 1215-cm⁻¹ vibration, it would indicate that the symmetry of the CO₂- substituent is not perturbed by the counterion, and one could then obtain the average rotation angle (δ) of the carboxylate group from a combination of expressions 6 or 7, i = b, and (9–11).

IR Measurements on Cd²⁺ [4]. Both the normal incidence and the grazing incidence absorbances were proportional to the number of layers in the film, except for the first layer. Results of normal incidence measurements were independent of the state of polarization of the light and all attempts to detect a deviation from uniaxial behavior failed. Results for multilayer assemblies are shown in Figure 8 (normal incidence) and Figure 9 (grazing incidence). Results for a monolayer are shown in Figure 10.

In all cases, peaks appear at the same locations as in the isotropic spectrum, which is also shown in Figure 8, but their intensity distribution is very different. The large relative suppression of the 1215-cm⁻¹ peak at the normal incidence and its relative enhancement at grazing incidence immediately demonstrate that the [n]staffane rods are standing up on the surface. The effect is particularly striking for the monolayer: in Figure 10, the 1215-cm⁻¹ peak is nearly absent at normal incidence (Ge substrate) and the 2870- and 2905-cm⁻¹ peaks are not detectable at grazing incidence (Au substrate). The relative intensity of the single terminal CH stretch near 2980 cm⁻¹ in the grazing incidence spectrum of Figure 10 contrasts eloquently with the absence of any intensity for the stretching vibrations of the 24 C–H bonds in the CH₂ groups. In contrast, in the isotropic spectrum, the peak due to the terminal CH stretch is completely buried under the tail of the CH₂ stretching peaks.

Clearly, on the gold substrate, the [n]staffane rods in the monolayer are lined up essentially exactly (within 1°) perpendicular to the surface. On the germanium substrate, the average tilt is clearly larger. Comparison with Figures 8 and 9 demonstrates that in multilayer assemblies the tilt angle also differs from zero significantly.

Results of a quantitative evaluation of the ratios $Q_{d,dc}$ and $Q_{d,dG}$ are collected in Table I, which also lists the average tilt angles (α). The expected relation $Q_{d,dN} = Q_{d,dG} = 1$ is fulfilled well. The tilt angles in the multilayers derived from the grazing incidence measurements (22 ± 2°) agree with those derived from ellipsometry (15–35°) and X-ray deflection (12–21°). Those derived from normal incidence measurements deviate systematically toward somewhat larger values (28 ± 2°). We believe that the larger average tilt angle on the Ge surface is due to its relative roughness and does not necessarily reflect any intrinsic property of the L–B film on germanium.

The intensity ratios for the vibrations of the CO₂ group do not follow the expected pattern. In particular, the...
symmetric CO$_2^-$ stretch at 1440 cm$^{-1}$, which should have
the same $Q_{dN}$ and $Q_{dG}$ values as the CH$_2$ wag at 1215
cm$^{-1}$, has quite different values and it is obvious that its
average transition moment direction is perturbed by the
counterion and does not point along the [n]staffane axis.
Under these circumstances, it is pointless to try to interpret
the significance of the intensity ratios for both the CO$_2^-$
vibrations at the present time. Since there are two
molecules of I[4] for every Cd$^{2+}$ cation, it is quite likely
that there are two or more distinct carboxylate sites and
that the observations reflect a complicated average.

Conclusions

Salts of [n]staffane-3-carboxylic acids, n = 3 and 4, form
stable L-B films. In a monolayer, the [n]staffane rods
stand perpendicular to the surface on a gold substrate,
and probably on germanium as well. In a multilayer, they
pack at a tilt angle of about 20°, very similar to those
found in the single crystal of the [n]staffane hydrocarbons,
$n = 3$ and 4.

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21-3; Au, 7440-57-5.