calculations also confirm the relatively small differences in bioactivity of optical isomers.

Thus, our computational procedure offers an approach to evaluate alternative mechanisms and to rationalize observed bioactivities; it, as well, offers guidance for the design of new potent suicide inhibitors. A noteworthy finding in regard to the last point is that there is a large space available in the hydrophobic pocket that could accommodate yet bulkier and more hydrophobic substituents. While such molecular alterations might be beneficial to the binding characteristics of these lactones (K_i), it might be detrimental to their rate of inactivation (k_2). The conflicting effect brought about by such changes in substrate size and shape should be properly considered in designing new catalytic inhibitors.

Supplementary Material Available: Figures of three non-covalent substrate complexes (structure I), four acyl enzyme alkylation complexes (structure II), and six suicide compounds (structure III), as well as the coordinates for all figures (50 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Supermonomolecular Structure in the Langmuir–Blodgett Films of a Surface-Active Dye–Fatty Acid Mixed System

Yasujiro Kawabata,* Tatsuo Sekiguchi, Motoo Tanaka, Takayoshi Nakamura, Hideo Komizu, Koichi Honda, and Eiichiro Manda

National Chemical Laboratory for Industry
Yatabe, Ibaraki 305, Japan

Mitsuyoshi Saito, Michio Sugi, and Sigeru Iizima

Electrotechnical Laboratory
Sakura-mura, Ibaraki 305, Japan

Received April 10, 1985

A few studies have appeared on the construction of a supermonomolecular layer, defined as a complex layer upon the surface of water that involves more than one monolayer to form a supermonomolecular structure.[1-3] It will be very useful in expanding the technique of Langmuir–Blodgett (LB) films to construct such a supermonomolecular layer that is capable of being deposited on a substrate to form a unique structure.

We have found that a layer obtained under higher pressure, so far considered as a "collapsed" film, retains an ordered structure and that the deposition of this film results in an LB film with a unique bilayer unit structure. We also found that it is now possible to prepare and transfer either one monolayer or a bilayer of a surface-active dye–fatty acid mixed system merely by the control of the surface pressure (Π). Preliminary results are given here.

The synthesis of a squarylium dye, 2,4-bis[(3,3-dimethyl-1-octadecyl-2(3*H*)-indolylidene)methyl]-1,3-cyclobutadienediylium-1,3-diolate (1) was accomplished by a modified

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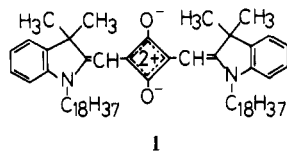
procedure in the literature.[4] Eicosanoic acid (2) was purchased from Eastman Kodak Co. and used without further purification. Π–*A* isotherms were measured by using a Lauda Filmwaage on an aqueous solution of 4.0×10^{-4} M $CdCl_2$ and 5.0×10^{-5} M $KHCO_3$ at 17 °C and pH 6.0. Chloroform was used as a
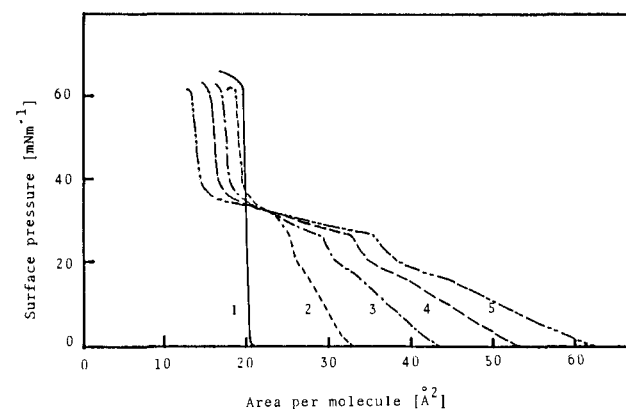
Figure 1. Surface–pressure isotherms of monolayers curves 1–5; surface pressure vs. area per **2** molecule (curve 1) and mixed films of **1** and **2** of molar mixing ratio r (r = 1:10, curve 2; r = 1:5, curve 3; r = 1:3, curve 4; r = 1:2, curve 5).

spreading solvent. The thickness of LB films was determined by the stylus method. The instrument used was a Taylor-Hobson Talystep with a tip radius of 12.5 μm and the stylus force was 2 mg.

Π–*A* isotherms of mixed monolayer of **1** and **2** with molar ratios ranging from 1:10 to 1:2 showed that two "collapse" points (by the conventional explanation[5]) are seen at 30 and up to 60 mN m^{-1} (Figure 1). We assumed that these points represent the occurrence of two condensed states and calculated the area of **1** at 25 and 40 mN m^{-1} on the assumption that the area of **2** per molecule of mixed monolayer is the same as in pure monolayer. The calculated area per molecule of **1** is 70 Å^2 and nearly 0 Å^2 at 25 and 40 mN m^{-1}, respectively. The latter value is unusual in view of the fact that **1** has two long alkyl chains. However, we can rule out the possibility of **1** being dissolved into the subphase. The addition of NaCl ranging from 1×10^{-3} to 5×10^{-3} M also afforded the same values for the areas per molecule of **1** at both 25 and 40 mN m^{-1}. In addition, for the case of r = 1:5, the optical density of **1** at 640 nm (λ_{max} for the main peak) of the deposited films at 40 mN m^{-1} (HPF) was about twice those of the films at 25 mN m^{-1} (LPF). These results show that a mixed monolayer is formed at 25 mN m^{-1} and that **1** is squeezed out from the monolayer of **2** at around 40 mN m^{-1} to form a complex layer, whose Π–*A* behavior is governed by **2** alone.

Mixed films of **1** and **2** (r = 1:5) were deposited at 25 and 40 mN m^{-1} on a slide glass as typical Y films, and in each case the apparent transfer ratios for both the downward and the upward strokes were between 1.0 and 1.1. The values of electric capa-

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Figure 2. Nominal layer number vs. thickness of LB films (O) mixed film of **1** and **2** of molar ratio *r* (*r* = 1:5) deposited at 25 mN m⁻¹; (●) mixed films of **1** and **2** (*r* = 1:5) at 40 mN m⁻¹; (▲) films of pure **2** at 25 mN m⁻¹; (■) films of pure **2** at 40 mN m⁻¹.

citance of the LPF were 1.5 times larger than those of the HPF for the same layer numbers, which also showed that HPF are thicker than LPF. The thickness of various types of LB films with four different stroke numbers from 21 to 81 were measured by the stylus method (Figure 2). HPF were twice as thick as LPF, while the thickness of LPF and pure **2** deposited at 25 or 40 mN m⁻¹ coincided with one another. This relationship holds for the case of the smaller fraction of **1**, [**1**]:[**2**] = 1:10. In this case, it is apparent that **1**, if squeezed out from a monolayer of **2**, cannot cover the whole area of **2** in the complex layer.

From the facts described above, we may conclude that **1** is squeezed out to form islands, each serving as a pillar between two monolayers of **2** in HPF, hence the thickness of unit layer of HPF is increased to be twice that of LPF. The study of the detailed structure is in progress.

Registry No. 1, 97521-39-6; **2**, 506-30-9.

Duality of Mechanism, Radical and Nonradical, in the Dehalogenation of Aryl Halides by Lithium 2,6-Dimethylpiperidide[1]

Jerzy Winiarski[2] and Joseph F. Bunnett*

*Department of Chemistry, University of California
Santa Cruz, California 95064*

Received April 26, 1985

Metal derivatives of dialkylamines sometimes effect hydrodehalogenation[3-8] of aryl halides. A variety of mechanisms, all of ionic type, have been proposed.

Alkoxide ions also dehalogenate aryl halides; a radical chain mechanism appears to prevail.[9-11] We visualized the possibility

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Scheme 1

Table 1. Reactions of Lithium 2,6-Dimethylpiperidide with Aryl Halides in 2,6-Dimethylpiperidine Solution

ArX	other substance	temp	time, h	prod mix ArX[a]	ArH	5 or 6
3i	nil	rt[b]	1	57	37	**5**, 1%
3i	(*t*-BuO)₂[c]	rt	1	18	63	nil
3i	Ph₂C=CH₂[d]	rt	1	72	18	**5**, 8%
3i	PhN=NPh[c]	rt	1	76	10	**5**, 4%
3c	nil	reflux	2	43	26	**5**, 17%
3c	(*t*-BuO)₂[c]	reflux	2	54	36	**5**, 4%
3c	Ph₂NNPh₂[d]	reflux	2	35	53	**5**, 5%
3c	Ph₂C=CH₂[d]	reflux	2	46	20	**5**, 21%
4i	nil	rt	1	95	5	nil
4i	(*t*-BuO)₂[d]	rt	1	72	27	nil
4i	nil	reflux	0.5	16	72	nil
4i	12-crown-4[e]	reflux	0.5	87	9	nil
4b	nil	reflux	2	49	33	**6**, 5%
4b	Ph₂C=CH₂[f]	reflux	2	60	16	**6**, 10%
4b	Ph₂NNPh₂[d]	reflux	1	45	45	*g*
4b	12-crown-4[e]	reflux	1	96	4	*g*

[a] Recovered, unreacted ArX. [b] rt = room temperature. [c] 20 mol %. [d] From 6 to 11 mol %. [e] 100 mol %. [f] 57 mol %. [g] Not sought.

that the dehalogenation by metal derivatives of amines might occur by a similar sort of mechanism, the salient features of which are shown in Scheme I.

In Scheme I, step 1, a radical abstracts a hydrogen atom from C-1 of the amide ion, generating radical ion **1**. **1** is the radical anion of an imine. Steps 2, 3, and 4 constitute a propagation cycle; in (2) an electron is transferred from **1** to the aryl halide, in (3) the resulting radical anion fragments to form the corresponding aryl radical, and in (4) the aryl radical abstracts hydrogen from C-1 of the amide, to regenerate **1**. The amide ion may be free or associated with Li⁺, even covalently. Termination steps are implied.

For our experiments, we chose to use lithium 2,6-dimethylpiperidide (**2**) as the amide reagent and two types of aryl halides

unable to afford aryne intermediates as test substrates: 1-halo-2-methylnaphthalenes (**3**) and mesityl halides (**4**). On treatment with **2**, in *cis*-2,6-dimethylpiperidine solution, substrates **3** and

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