

The same questions of vibrational excitation and quenching arise. The 193-nm photon has about 150 kcal and breaks a 75-kcal bond. Hence 75 kcal of internal excitation is shared between V* and Br*. The latter cannot have more than 10 kcal of electronic excitation so that V* may share 65 kcal with Br. Their half-life, using $\sim 10^{14}$ HCl is, about 1.5 ms and is measured by their loss, not by C₂H₄ production. It is difficult to know what role excited V* plays in their system, either in the chemical reaction or in the mass spectrometer detection where threshold photoionization is used to produce mass 27 cations. In 1.5 ms there are about 2500 collisions of V* with He, a very poor vibrational quencher. Most disconcerting is the fact that a rate constant of about 100 s⁻¹ is attributed to some unknown wall reaction of vinyl radicals. This accounts for from 25 to 50% of the total loss of vinyl.

In the VLPR system, all species are under observation and mass balances can be done to a few percent on all species. This is not the case in the flow systems where unknown wall reactions remove up to half of the radicals in times competitive with the reaction times.

The carrier gas He is a notoriously poor quencher of vibrational energy, particularly for species with small excitations in any given mode. Hence there is very little guarantee that one is not dealing with vibrationally excited radicals. This internal energy may affect their reactivity and also their detectability in the mass spectrometric system which depends on threshold photoionization to produce ions. It may be that excited radicals have a larger ion-

ization cross-section than ground-state species. In this case, there could be a systematic bias in detectability as initially produced radicals are collisionally quenched during the course of the reaction. This could contribute to the mysterious wall loss of radicals. Such an effect could also show a systematic variation with temperature.

If in our system radicals disappeared on the walls with rates comparable to this, we should never have seen ethyl radicals, and none of the subsequent reactions reported would have occurred. In our 2-mm orifice, residence times of radicals are about 2 s so that wall rates of 10–200 s⁻¹ would have precluded observations of any radicals or radical reactions.

In the earlier Cl/C₂H₄ study³ where equilibrium was observed by adding HCl, some studies were made with an initial ratio (HCl)₀/(Cl)₀ \sim 2.2, and (Cl) consumption was followed to extents of 50% and 60%. This would not have been possible if k_{-4} were two to four times larger than we have measured. In this equilibrium study there would have to have been collective errors in the concentrations of C₂H₄, Cl, and HCl amounting to 400 and 200% for such an error to occur. This is simply not possible in view of the excellent mass balances observed.

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Langmuir–Blodgett Film Assembly of Novel Dye Molecules Substituted by a Steroid Skeleton: Molecular Design for Uniform Films

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Abstract: Amphiphiles including dye skeletons such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), *p*-phenylenediamine (PD), *p*-quinonediimine (QI), tetrathiafulvalene (TTF), *p*-benzoquinone (BQ), and anthraquinone (AQ) were newly synthesized to obtain a design rule to produce uniform LB films. The amphiphiles were divided into four groups, based on the differences in hydrophobic tails: monoalkyl derivatives (group 1); *tere*-dialkyl or *tere*-tetraalkyl derivatives (group 2), where long alkyl chains were attached to the dye skeleton at separate locations; *ortho*-dialkyl derivatives where two alkyl chains were attached to the dye skeleton at adjacent locations (group 3); and steroid derivatives (group 4). The amphiphiles including large dye moieties in groups 1 and 2 generally formed unstable monomolecular films on a water surface, if their hydrophilic properties were weak. The latter two groups, whose hydrophobic tails could be closely packed together, yielded stable and condensed monomolecular films. The films for group 3, however, indicated high surface viscosity values (> 1 g/s at 10 dyn/cm), resulting in inhomogeneous LB films. Group 4 molecules yielded less viscous films, resulting in homogeneous LB films. Furthermore, introducing a large and/or strong hydrophilic head into group 3 or 4 compounds was effective for decreasing the viscosity values (10^{-1} – 10^{-2} g/s) and producing homogeneous LB films. The geometric sizes and molecular cohesions of the amphiphiles were found to have great influence on the film-forming properties. Optimum molecular structures for producing uniform dye LB films were discussed.

Introduction

The Langmuir–Blodgett (LB) method¹ has long been known as a technique for use in constructing organic thin films with high-order molecular arrays or superlattices with different kinds of molecules. A wide range of applications using LB films, including various functional molecules, have been proposed.²

However, the presence of structural inhomogeneities and micro-defects in the built-up films on metal or semiconductor substrates has recently been revealed.³ Furthermore, LB films are rather

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unstable and are apt to change into three-dimensional crystals.⁴ These factors prevent fabricating the tailored molecular assemblies and realizing their applications, particularly in an electric field. Therefore, one of the key subjects in this method has been the building up of uniform and stable LB films, including various functional dye skeletons.

In this connection, a lot of functional dye molecules with amphiphilic substituents have been synthesized.⁵ These include donor and acceptor skeletons, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), *p*-phenylenediamine (PD), *p*-quinonediimine (QI), tetrathiafulvalene (TTF), *p*-benzoquinone (BQ), and anthraquinone (AQ).⁶ Unfortunately, a considerable part of the synthesized dye amphiphiles possess poor film-forming properties, reflecting their inappropriate molecular structures. As a result, they have been employed as diluted mixtures with other effective film-forming amphiphiles like fatty acids. Some substantial problems, however, regarding inhomogeneous dispersion and low molecular density for dye molecules still remain.⁷

The situation mentioned above is considered mainly to be rooted in the uncriticized and simple idea for designing LB molecules: introducing long alkyl chains and/or hydrophilic heads into main source dye skeletons. There have been efforts to determine the pertinent relations between molecular structures and their film-forming properties. Stewart⁸ and Steven et al.⁹ synthesized a wide range of anthracene derivatives with linear alkyl chains of different lengths and with different hydrophilic heads. Taylor and Holden et al. reported fluorenylidene¹⁰ and carbazole derivatives¹¹ with different kinds of hydrophobic tails, such as monoalkyl, dialkyl, unsaturated alkyl, and branched alkyl groups. Metzger et al. synthesized TCNQ and nitrobenzene derivatives with mono-, di- and trialkyl chains.¹² These workers successfully produced the dye LB films without matrix molecules. However, these attempts, in most cases, have been concerned only with the particular molecules, and hence the findings are limited for them. Therefore, a unified design rule applicable to various dye amphiphiles for uniform LB films has not yet been well established.

A uniform and stable condensed monomolecular film on a water

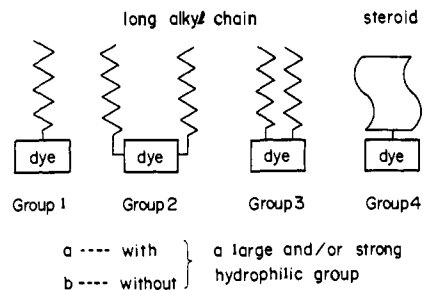
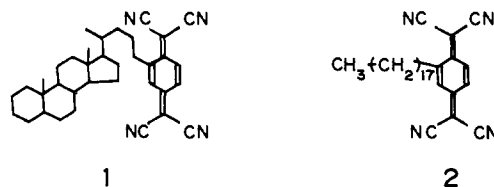


Figure 1. Models of amphiphiles used in this study.

surface is indispensable for constructing a good-quality LB film. Thus, the monomolecular film behaviors, such as homogeneous fluidity and stability during compression, are essentially important. As is well known, surface viscosity for a monolayer on a water surface is a primary factor.¹³ Many workers have investigated monolayer viscosities for fatty acids and their analogues. They have reported the effects of alkyl chain lengths, of alkyl chain configurations, of hydrophilic head variations, and of metal ions added to a water phase.¹⁴ However, there have been few works reported about the monomolecular film viscosities in relation to the molecular structures of the dye amphiphiles.

In a previous paper,¹⁵ we reported results of systematically investigating the relations between molecular structures and monomolecular film properties, including surface viscosities, micromorphologies, and film transfer characteristics, exemplified by fatty acids possessing various hydrophobic tails. Two molecular factors, geometric size and cohesive interaction, were found to affect the monolayer properties. We also proposed a new amphiphilic model structure, consisting of a steroid tail and a strong and/or large hydrophilic head for producing homogeneous monomolecular films with low surface viscosities. According to this prediction, we succeeded in obtaining a new TCNQ derivative (1) substituted by a steroid tail,¹⁶ which was the first example of steroid dye molecules producing uniform LB films. The findings suggest that the structural model, based on geometric size and molecular cohesion, represents an optimal design rule for producing uniform dye LB films.



In the present study, we have synthesized various dye amphiphiles classified into eight groups (groups 1a–4b), as shown in Figure 1, according to the geometric sizes of hydrophobic, dye, and hydrophilic parts and to the strength of their cohesive interactions. The monomolecular film properties (stability, surface viscosity, and transfer property) have been investigated to verify the general structural design rule for dye amphiphiles.

Results

Synthesis. The synthetic routes leading to the dye amphiphiles are shown in Figures 2–5. In Figure 2, eight *p*-phenylenediamine (PD) amphiphiles with different hydrophobic tails and hydrophilic heads (3–10) were shown. *N,N*-Dioctadecyl PD (5) was obtained

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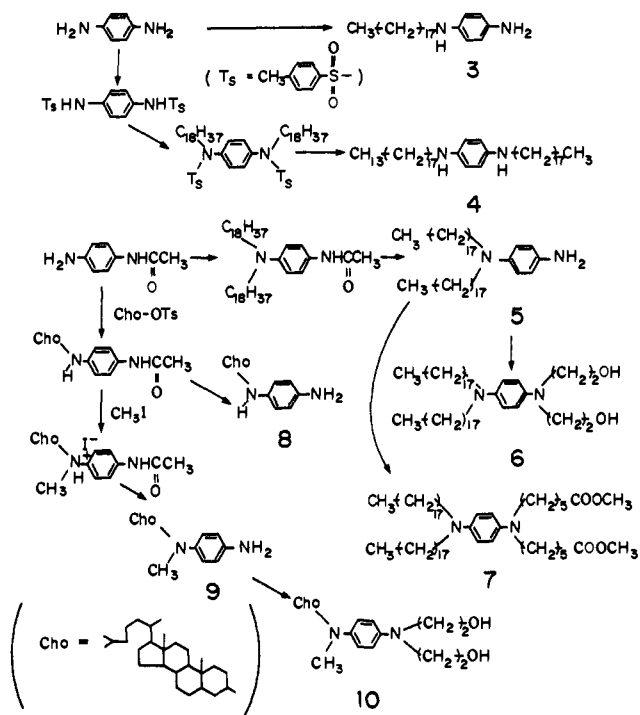


Figure 2. Synthetic routes and chemical structures of *p*-phenylenediamine (PD) amphiphiles.

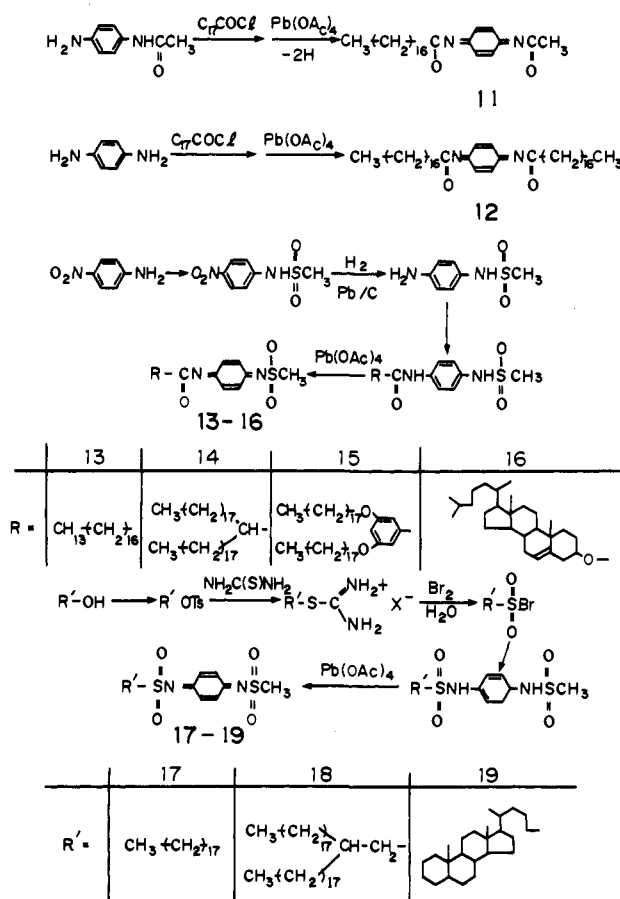


Figure 3. Synthetic routes and chemical structures of *p*-quinonediimine (QI) amphiphiles.

in a high yield, according to the synthetic method¹⁷ of *N,N*-dihexadecyl PD. *N*-Cholestan-3-yl PD (8) was obtained from cholesterol-3-yl tosylate in a low yield, because the substitution

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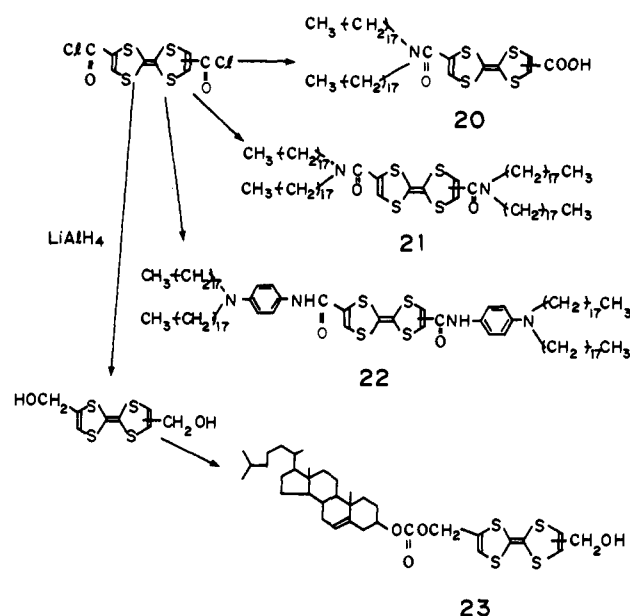


Figure 4. Synthetic routes and chemical structures of tetrathiafulvalene (TTF) amphiphiles.

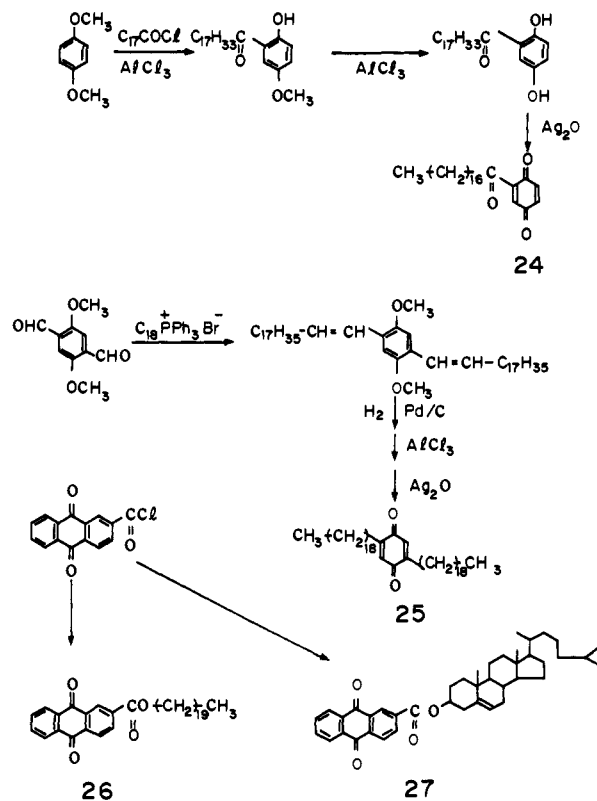


Figure 5. Synthetic routes and chemical structures of *p*-benzoquinone (BQ) and anthraquinone (AQ) amphiphiles.

reaction was seriously inhibited by the elimination of the secondary tosylate. In the synthesis of *N*-Cholestan-3-yl-*N*-methyl PD (9), an excess amount of methyl iodide was added at once to avoid quaternary ammonium formation. Most PD derivatives listed in the figure were isolated as their hydrochloride salts, which could then be purified.

N,N'-Dicyano-*p*-quinonediimine (QI)¹⁸ is known to be an acceptor as strong as TCNQ. From the cyclic voltammetry results, *N,N'*-diacetyl QI indicated a similar redox potential to that for *p*-benzoquinone. The electron-accepting capability of *N,N'*-dimethanesulfonyl QI corresponded approximately to that of

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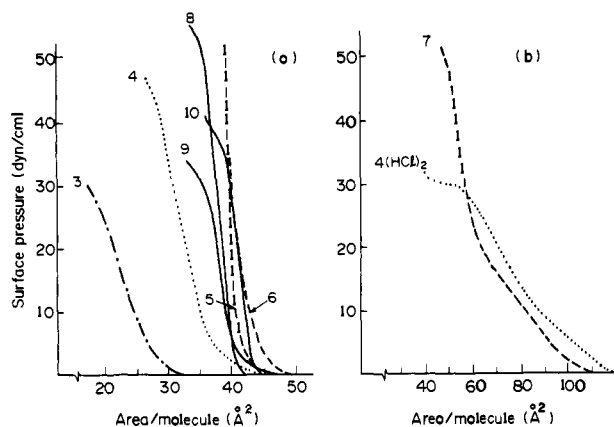


Figure 6. Surface pressure (π)-area (A) curves of *p*-phenylenediamine (PD) amphiphiles on pure water at 18 °C.

chloranil (tetrachloro-*p*-benzoquinone).¹⁹ We have synthesized *N,N'*-diacyl, *N*-acyl-*N'*-sulfonyl, and *N,N'*-disulfonyl QI amphiphiles 11–19, as shown in Figure 3. All the QI derivatives were obtained from the corresponding *p*-phenylenediamide derivatives, by dehydrogenation using lead tetraacetate, according to pertinent literature.²⁰ For the synthesis of *N,N'*-disulfonyl QI amphiphiles 18 and 19, the sulfonyl bromide yields were somewhat low. This is because of inhomogeneous reaction conditions, where hydrophobic reactants were admixed in an aqueous solvent.²¹

In Figure 4, four tetrathiafulvalene (TTF) amphiphiles (20–23) synthesized were shown. The source compound TTF dicarboxylic acid was obtained by a similar route described in pertinent literature.²² *p*-Benzoquinone (BQ) (24, 25) and anthraquinone (AQ) amphiphiles (26, 27) were also synthesized according to the routes in Figure 5.

Classification and Thermal Properties of Synthesized Amphiphiles. In Table I, the amphiphiles employed were classified into four groups (groups 1–4) based on the differences in hydrophobic tails: monoalkyl derivatives (group 1); *tere*-dialkyl or *tere*-tetraalkyl derivatives (group 2) where long alkyl chains were attached to the dye skeleton at separate locations; *ortho*-dialkyl derivatives where two alkyl chains were attached to the dye skeleton at adjacent locations (group 3); and steroid derivatives (group 4). The amphiphiles were further classified into eight groups, based on the hydrophilic heads: with (groups 1a–4a) and without a strong and/or large hydrophilic head (groups 1b–4b).

Melting points of the amphiphiles prepared here are also summarized in Table I. The melting points for the dialkyl amphiphiles were generally lower than those for the corresponding monoalkyl amphiphiles, while the steroid amphiphiles had higher melting points than the long alkyl derivatives. Hence, amphiphiles with steroid tails have improved thermal stabilities.

The enthalpy ($-\Delta H_m$) and entropy changes (ΔS_m) of melting for the amphiphiles also reflected their molecular structures. It was found that the mono- and dialkyl derivatives had larger $-\Delta H_m$ and ΔS_m values than the steroid ones, as shown in Table I. Relatively large enthalpy values of melting indicate strong molecular cohesions of the derivatives in their solid states. Thus, the cohesions of the steroid amphiphiles were rather weak, compared with those of the long alkyl amphiphiles. The weak cohesions of the steroid amphiphiles were found to interrelate to the weak molecular aggregation at air/water interfaces. Therefore, it caused smaller monolayer surface viscosities, as described later.

Hydrophilic and Hydrophobic Properties of Synthesized Amphiphiles. Hydrophilic and hydrophobic properties of the am-

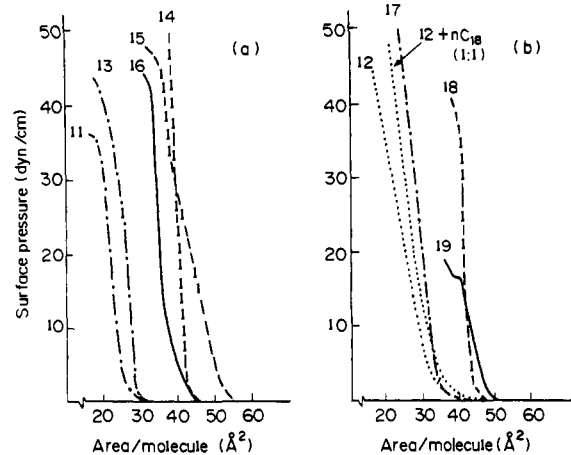


Figure 7. Surface pressure (π)-area (A) curves of *p*-quinonediimine (QI) amphiphiles on pure water at 18 °C. nC_{18} means *n*-octadecane.

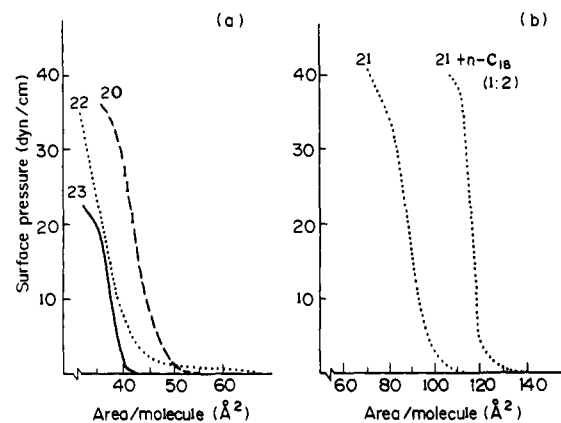


Figure 8. Surface pressure (π)-area (A) curves of tetrathiafulvalene (TTF) amphiphiles on pure water at 18 °C. nC_{18} means *n*-octadecane.

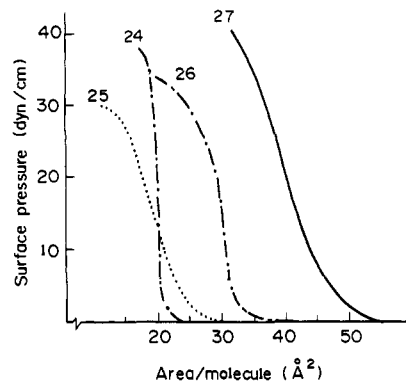


Figure 9. Surface pressure (π)-area (A) curves of *p*-benzoquinone (BQ) and anthraquinone (AQ) amphiphiles on pure water at 18 °C.

phiphiles can be estimated from R_f values of thin-layer chromatography (TLC). Small R_f values obtained by using hydrophilic silica gel plates and hydrophobic organic eluents, such as chloroform, usually indicate strong hydrophilic properties of the amphiphiles. The R_f values of the amphiphiles increased in the following order: monoalkyl amphiphiles < steroid ones < dialkyl ones; for example, $R_f = 0.72$ (3) < 0.76 (9) < 0.86 (5), as shown in Table I. Therefore, the hydrophilic properties can be considered to decrease in the above order.

Force-Area Curves and Monolayer Stabilities. The monoalkyl and *tere*-dialkyl amphiphiles, including the dye moieties with large cross-sections in groups 1 and 2 generally formed unstable monomolecular films on a water surface and easily collapsed during compression, when their hydrophilic properties were weak. The *ortho*-dialkyl and steroid amphiphiles (groups 3 and 4), whose hydrophobic groups had larger cross-sections, yielded stable and

(19) The redox potentials were measured by the cyclic voltammetry ($CH_2Cl_2/0.1$ M $n-Bu_4N^+BF_4^-/Pt$ vs $Ag/AgCl/CH_3CN$): *N,N'*-dimethanesulfonyl QI, 0.18 V; *N,N'*-diacetyl QI, -0.22 V (reference chloranil, 0.24 V; benzoquinone, -0.32 V).

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Table I. Classification and Thermal Properties of the Dye Amphiphiles

dye	compd	group ^a	R _f ^b of TLC	mp (°C)	-ΔH _m (kcal/mol)	ΔS _m (cal/deg·mol)
TCNQ	1	4b	0.27	188	6.85	14.9
	2	1b	0.29	125	12.2	30.6
PD	3	1b	0.72	82		
	4	2b	0.83	100		
	5	3b	0.86	41	24.7	78.6
	6	3a	0.75	58	17.7	53.5
	7	3a	0.92	20		
	8	4b		124		
	9	4b	0.76	116		
	10	4a	0.71	172	3.2	7.2
	11	1b	0.18	92		
diacyl QI	12	2b	0.40	106		
	13	1b	0.24	90		
acylsulfonyl QI	14	3b	0.54	62		
	15	3b	0.40	40		
	16	4b	0.28	120 dec		
disulfonyl QI	17	1b	0.28	127		
	18	3b	0.69	76		
	19	4b	0.42			
TTF	20	3b	0.01	70		
	21	2b	0.41	75		
	22	2b	0.49	156		
	23	4b		150 dec		
BQ	24	1b		95		
	25	2b		100		
AQ	26	1b		106	18.0	47.5
	27	4b		164	3.5	8.0

^aKey: 1, monoalkyl; 2, *tere*-dialkyl or tetraalkyl; 3, *ortho*-dialkyl; 4, steroid derivatives, with (a) and without a large and/or strong hydrophilic group (b). ^bElution solvent: dichloromethane for TCNQ, ethyl acetate for PD, and chloroform for QI and TTF amphiphiles.

Table II. Monolayer Properties of the Dye Amphiphiles

compd (group)	A _{π→0} ^a (Å ²)	molecular ^b area at collapse (Å ²)	film ^b collapse pressure (dyn/cm)	film ^c stability	surface ^d viscosity (g/s)	Δπ ^e (dyn/cm)
1 (4b)	46	42	16	st	0.15	
2 (1b)	19			no		
3 (1b)	28	20	26	un		
4 (2b)	37			no		
4 (HCl) ₂ (2a)	100	58	28	ex		
5 (3b)	41	40	>50	st	>10	23.3 (23.7)
6 (3a)	44	40	37	st	0.75	
7 (3a)	67, 102 ^f	50	47	ex		
8 (4b)	41	36	49	st		
9 (4b)	41	37	26	st	0.76	
10 (4a)	43	40	34	st	0.088	
11 (1b)	25	20	33	st		
12 (2b)	33			no		
12 + C18 ^g (1:1)	34			no		
13 (1b)	29	24	32	st	0.25	
14 (3b)	42	39	50	st	1.7	14.5 (21.7)
15 (3b)	45, 52 ^h	37	44	st	0.21	3.2 (24.0)
16 (4b)	38	34	43	st	0.20	1.4 (24.4)
17 (1b)	34	26	40	un		
18 (3b)	42	41	33	st	>10	
19 (4b)	48	40	16	st	0.003	
20 (3b)	56	40	30	st	>10	44.5 (44.0)
21 (2b)	97	82	33	st		
21 + C18 (1:2)	121	113	36	st		
22 (2b)	42			no		
23 (4b)	40	37	18	st	10	
24 (1b)	21	20	29	st		7.7 (23.6)
25 (2b)	24			no		
26 (1b)	32	29	20	un		
27 (4b)	46	37	32	st		

^aObtained by the extrapolation of the linear surface pressure (π)-area (A) plots of the condensed films to the intercept. ^bValues where the slope (-dπ/dA) began to decrease. ^cKey: st, stable; un, unstable; no, no monolayer; ex, expanded. ^dMeasured at 18 °C at 10 dyn/cm with a canal viscometer. ^eValues in the parentheses mean the static surface pressure values (π_{sub,s}) prior to substrate dipping. ^fAn inflection appeared at about 65 Å²/molecule at 20 dyn/cm. ^gn-Octadecane. ^hAn inflection appeared at 39 Å²/molecule at 30 dyn/cm.

condensed monomolecular films. The monolayer properties are summarized Table II. Molecular areas (A_{π→0}) were obtained by the extrapolation of the linear surface pressure (π)-area (A) plot for the condensed film region to the intercept in the π-A curves, measured on a pure water surface at 18 °C (Figures 6-9). The collapse points were determined as the points where the slope (-dπ/dA) began to decrease.

Figure 6 indicates π-A curves of the PD amphiphiles 3-10. Compounds 5, 6, and 8-10 belonging to group 3 or 4 gave steep π-A curves and formed stable and condensed monomolecular films up to 25-50 dyn/cm, showing the A_{π→0} value of 41-44 Å². The collapse areas of the steroid (5α-cholestan-3β-yl) amphiphiles 8, 9, and 10, however, were slightly smaller than those of the dialkyl ones (5, 6). The result was in agreement with the fact that the

$A_{\pi=0}$ value of 5 α -cholestan-3 β -ol was 38–39 \AA^2 , which is slightly smaller than the cross-section of the dialkyl chain (40 \AA^2). No hysteresis was observed in continuous compression and expansion procedures. The amphiphiles with two hydroxy groups (6, 10) showed larger $A_{\pi=0}$ values (44, 43 \AA^2) than those (41 \AA^2) without them (5, 8, 9). The dialkyl PD with two methyl carboxylate groups (7) produced an expanded film due to its low melting point (20 $^{\circ}\text{C}$). The monoalkyl PD 3 produced an expanded π - A curve, and its compressed film was unstable. The *tere*-dialkyl compound 4 belonging to group 2b did not produce a monomolecular film, but probably folded multilayers. The hydrochloride adduct of 4 (group 2a) produced an expanded monomolecular film, which was collapsed at 58 \AA^2 /molecule.

Figure 7 indicates π - A curves for the QI amphiphiles 11–19. Compounds 14–16, 18, and 19 belonging to group 3 or 4 yielded stable monomolecular films at about 40–45 \AA^2 /molecule, as well as the PD amphiphiles. The monoalkyl compounds 11, 13, and 17 produced monomolecular films with closely packed areas of 25–30 \AA^2 /molecule, which were larger than that for the monoalkyl chain (20 \AA^2). The compounds including an *N,N'*-diacyl QI (11) or an *N*-acyl-*N'*-sulfonyl QI moiety (13) produced stable monolayers at 25 dyn/cm. The compound including a larger *N,N'*-disulfonyl QI moiety (17), however, produced an unstable monolayer. The *tere*-dialkyl QI 12 belonging to group 2b did not produce a monomolecular film. An equimolar amount of *n*-octadecane was added to the compound 12 film. The film area was slightly expanded; however a monomolecular film could not be obtained.

Figure 8 shows π - A curves of the TTF amphiphiles 20–23. Compounds 20 and 23 belonging to group 3 or 4 produced stable monomolecular films. The *tere*-tetraalkyl compound 21 belonging to group 2 yielded a monomolecular film, whose π values began to rise at 110 \AA^2 /molecule, and produced a closely packed stable film that was collapsed at 82 \AA^2 /molecule at 33 dyn/cm. The addition of double the molar quantity of *n*-octadecane to compound 21 expanded the film area, accompanied with a steeper slope of the π - A curve. The $A_{\pi=0}$ value (121 \AA^2) equaled the cross-section of six long alkyl chains. The other *tere*-tetraalkyl compound (22), synthesized from the dialkyl PD 5, did not yield a monomolecular film, decided from its smaller $A_{\pi=0}$ value (42 \AA^2) than the expected one (>80 \AA^2).

Figure 9 indicates π - A curves of the BQ and AQ amphiphiles 24–27. The monoalkyl compound, including a small BQ moiety (24) belonging to group 1, produced a stable monomolecular film. The monoalkyl compound including a large AQ moiety (26), however, yielded an unstable monolayer. The steroid AQ 27 produced a stable monolayer. The *tere*-dialkyl BQ 25 belonging to group 2b did not yield a monomolecular film as well as the *tere*-dialkyl PD and QI.

Among the steroid amphiphiles, the cholane amphiphiles 1 and 19 and cholic acid itself¹⁵ possessed larger occupied areas and lower collapse pressures than the cholestane (8–10) and cholestene amphiphiles (16, 23, 27).

Surface Viscosities. The surface viscosities of the amphiphile monolayers, measured with a canal viscometer at 18 $^{\circ}\text{C}$, were also shown in Table II. In the PD amphiphiles, the *ortho*-dialkyl compound 5 produced a less fluid monolayer with a viscosity value larger than 10 g/s. Introducing a steroid (9) or a large hydrophilic group, such as two hydroxy groups (6), into the source PD moiety reduced the viscosity to 0.76 or 0.75 g/s, respectively. The amphiphile 10 containing both the steroid and the two hydroxy groups showed a still further low viscosity of 0.088 g/s.

For the QI dye skeletons, dialkyl compounds 14 and 18 as well as the PD derivatives generally yielded monolayers with higher viscosity values than the steroid ones (16, 19) did. One of the dialkyl QI amphiphiles (15) produced a less viscous film, probably due to the fact that the two alkyl chains could not be closely packed at the observed surface pressure of 10 dyn/cm, as shown in Figure 7.

For the TTF moiety, both the dialkyl derivative 20 and the steroid one (23) produced viscous films, probably due to the strong cohesion of the TTF skeleton.

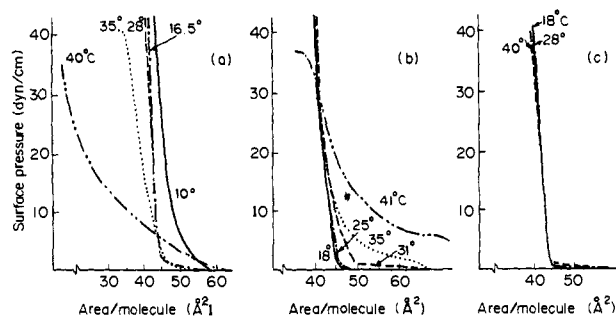


Figure 10. Temperature dependence of the π - A curves of *p*-phenylenediamine (PD) amphiphiles: (a) dialkyl PD 5, (b) dialkyl PD with two hydroxy groups (6), (c) steroid PD with two hydroxy groups (10).

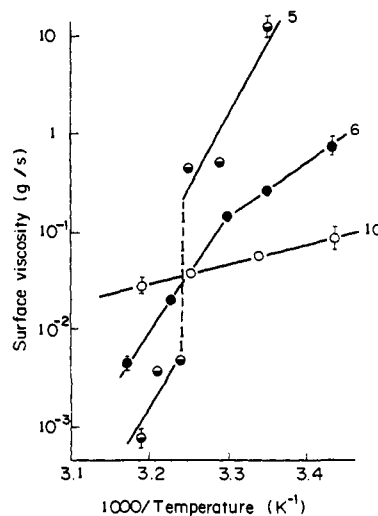


Figure 11. Arrhenius plots of the surface viscosities of *p*-phenylenediamine (PD) monolayers.

Subphase Temperature Influence on π - A Curves and on Surface Viscosities. Molecular cohesions of the amphiphiles on a water surface could be directly estimated by measuring temperature effects on the π - A curves and on the surface viscosities. Variations in subphase temperature caused great changes in the π - A curves and in the surface viscosities for the dialkyl PD amphiphiles 5 and 6, but caused small changes for the steroid PD amphiphile 10.

The dialkyl PD 5 monolayer melted above 36–37 $^{\circ}\text{C}$, corresponding to its power melting point (41 $^{\circ}\text{C}$), as shown in Figure 10a. The areas occupied in low temperatures were larger than those in high temperatures. This unusual result was due to film inhomogeneities in low temperatures. In temperatures lower than 25 $^{\circ}\text{C}$, surface viscosity was so large that it generated a wide surface pressure distribution.²³ The surface pressure value, observed at around the center of the two moving barriers, was larger than surface pressure values at other positions. In the low temperatures, furthermore, the microdomains were too hard to fuse into a homogeneous film within a short time of the compression procedure. The surface pressure value began to rise, when the domains conflicted with each other. Nevertheless, the bare water surface remained.¹⁵

The monolayer of the dialkyl PD with two hydroxy groups (6) changed to an expanded film above 30 $^{\circ}\text{C}$, as shown in Figure 10b. The π - A curve of the steroid PD 10, shown in Figure 10c, however, scarcely changed up to 40 $^{\circ}\text{C}$ (no measurement made above that temperature).

Figure 11 shows Arrhenius plots of the surface viscosity changes in the PD monolayers. The slope of the steroid PD 10 plot was smaller than the slopes of the dialkyl PD plots. In the plots of the dialkyl PD amphiphiles, a discontinuous point and an inflection

(23) (a) Egusa, S.; Nakayama, T.; Gemma, N.; Miura, A.; Azuma, M. *Thin Solid Films* 1989, 178, 165. (b) Miyano, K. *Langmuir* 1990, 6, 1254.

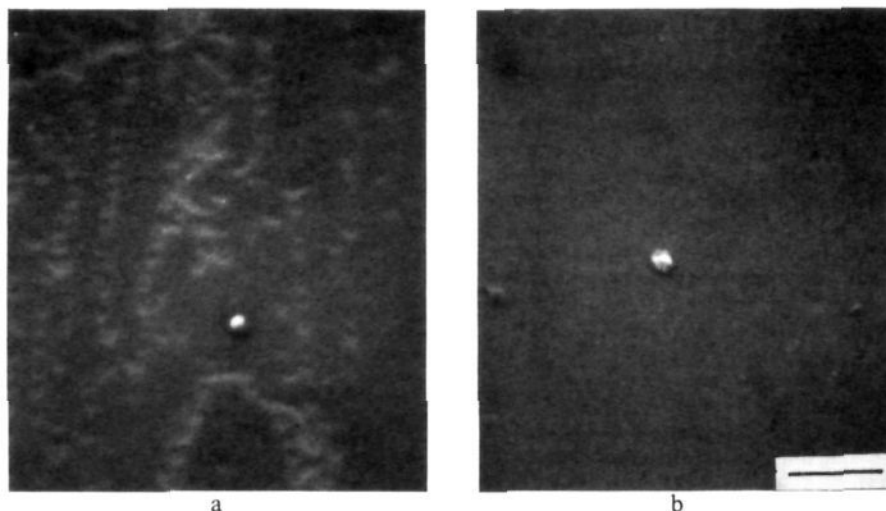


Figure 12. SEM images (a) of the dialkyl PD **5** bilayer and (b) of the steroid PD with two hydroxy groups (**10**) bilayer, deposited onto the methylated Si substrates. The SEM images were taken without metal coating at 1.5-kV accelerating voltage. The scale bar indicates 200-nm length. The white balls are dust.

point appeared at the temperatures where the films melted and expanded, respectively. Apparent activation energies for the dialkyl PD **6** in low temperatures and for the steroid PD monolayer **10** were 23 and 9.3 kcal/mol, respectively, which were roughly in accordance with the enthalpies of melting in the three-dimensional solid powders.

Film Transfer Properties and Transferred Film Homogeneities.

The *ortho*-dialkyl and steroid amphiphiles showed normal Y-type deposition. The *ortho*-dialkyl amphiphiles with large viscosity values, however, showed large surface pressure drops, resulting in inhomogeneous LB films. On the other hand, the steroid amphiphiles with small viscosity values produced homogeneous films. The monoalkyl amphiphiles with a large dye moiety showed Z-type or YZ-type deposition: The transfer ratios for the up-mode dipping were larger than those for the down-mode dipping.

We quantified film transfer properties by surface pressure drops ($\Delta\pi$),^{15,24} which were differences between the static ($\pi_{\text{sub,s}}$) and dynamic ($\pi_{\text{sub,d}}$) surface pressures at the substrate, prior to and during substrate dipping, respectively. Large $\Delta\pi$ values indicate monolayer packing looseness at the substrates during film transfer, resulting in inhomogeneous films.²⁵ Monolayer films with large viscosity values indicated large $\Delta\pi$ values, as shown in Table II.¹⁵ The dialkyl Pd **5** monolayer with the high viscosity value was able to be transferred onto solid substrates by the usual vertical dipping method at a dipping speed of 5 mm/min at 25 dyn/cm, detected by a Wilhelmy plate that was placed 3 cm away from the substrate. In this condition, the $\Delta\pi$ value was about 23 dyn/cm. The resulting LB film (bilayer) was inhomogeneous, and a lot of holes appeared, as shown in Figure 12a, even though the macroscopic transfer ratio was one unit. The $\Delta\pi$ value could be lowered by decreasing deposition speed:²⁴ 16.5 dyn/cm at 0.5 mm/min and 5.2 dyn/cm at 0.1 mm/min. It took an undesirable long time to build up multilayers.

The steroid PD **10** monolayer with the low viscosity value was able to be deposited onto a hydrophobic substrate by the vertical dipping method with a transfer ratio of one unit to yield a bilayer film, whose SEM image is shown in Figure 12b. The film surface was smooth, and no irregularity was observed. The dialkyl dye monolayers with large viscosity values (**14**, **18**, **20**), as well as PD amphiphiles, produced inhomogeneous films, while the steroid dye monolayers with low viscosity values (**16**, **19**) yielded homogeneous films, as determined by SEM observation.

The monolayer of the monoalkyl PD **3** could be transferred onto substrates after the area decrease almost ceased. The transfer

ratios at up strokes were larger than those at down strokes (YZ-type). The ratios, furthermore, were not constant, and varied within 1.0–1.1 for up strokes and within 0.7–0.9 for down strokes. The monolayer of the monoalkyl amphiphile, including a large AQ moiety (**26**), showed partial peeling off of the deposited monolayer at down strokes. The steroid AQ **27** monolayer showed YZ-type film transfer. The stable monolayers of the monoalkyl QI **11** and **13** and BQ **24** could be normally transferred.

Discussion

Molecular Structures and Monomolecular Film Stability. According to the CPK molecular models of the PD amphiphiles, shown in Figure 13, the monoalkyl chain of compound **3** is not large enough to prevent adjacent PD moieties from interacting strongly with each other. The dialkyl group and the steroid tail are large enough to eclipse the PD moiety. The monoalkyl amphiphiles, including a large dye moiety like TCNQ **2**, *N,N'*-disulfonyl QI **17** and AQ **26** as well as PD **3**, did not produce stable monolayers. The dialkyl and steroid amphiphiles, including the dye moieties, were able to produce stable monolayers. According to the CPK models, the cross-section of 5 β -cholane (AB ring junction of the steroid is *cis*) is larger than that of 5 α -cholestane (all ring junctions of the steroid are *trans*) and is larger than that of cholestene. This is one of the reasons why the cholane amphiphiles **1** and **19** and cholanic acid itself¹⁵ possessed larger occupied areas and lower collapse pressures than the cholestane (**8**–**10**) and cholestene amphiphiles (**16**, **23**, **27**). In pertinent literature, dialkyl compounds (group 3), including AQ,⁶⁸ ferrocene,²⁶ dipyrindinium ion,²⁷ styryl-pyridin,²⁸ fluorenylidene,¹⁰ and cinnamoyl ester,²⁹ yielded stable monolayers.

In the model of the *tere*-dialkyl compound **4** (group 2b), however, a vacancy appears between the long alkyl chains, when the PD moiety lies flat on a water surface. Such vacancies also exist in the models of the other group 2b compounds (**12**, **21**, **22**, **25**). It was difficult for such molecules to form stable monomolecular films in such conformations, if their hydrophilic properties were weak. Particularly, compounds **4**, **12**, **22**, and **25** did not produce monomolecular films on a water surface. Compound **21** yielded a monomolecular film, but the vacancy almost disappeared in its closely packed film. In pertinent literature, *tere*-dialkyl group 2b compounds including carbazole,^{7a} indigo,³⁰

(26) Nakahara, H.; Fukuda, K.; Sato, M. *Thin Solid Films* **1985**, *133*, 1.

(27) Fujihira, M.; Nishiyama, K.; Aoki, K. *Thin Solid Films* **1988**, *160*, 317.

(28) Möbius, D.; Cordroch, W.; Loschek, R.; Chi, Li Feng; Dhathathreyan, A.; Vogel, V. *Thin Solid Films* **1989**, *178*, 53.

(29) Laschewsky, A.; Ringsdorf, H.; Schmidt, G. *Thin Solid Films* **1985**, *134*, 153.

(30) Vikholm, I.; Helle, H. *Thin Solid Films* **1989**, *178*, 197.

(24) Nakayama, T.; Egusa, S.; Gemma, N.; Miura, A.; Azuma, M. *Thin Solid Films* **1989**, *178*, 137.

(25) Nakayama, T.; Miura, A.; Azuma, M. *Thin Solid Films* **1989**, *178*, 477.

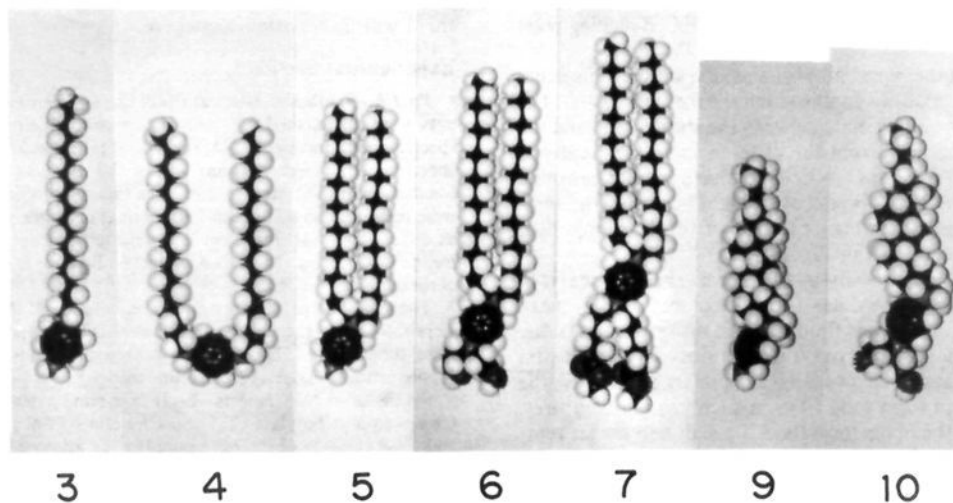


Figure 13. CPK molecular models of *p*-phenylenediamine (PD) amphiphiles.

and divinylbenzene³¹ did not yield stable monolayers.

Therefore, the following geometric relationship would be necessary for stable monolayers: $Sh \approx Sd$, where Sh means the cross-section of hydrophobic groups, and Sd means the cross-section of a dye. The similar geometrical requirement has already been pointed out by many other workers, who introduced plural,^{10,12} branched,¹⁰ and cis-unsaturated alkyl chains¹⁰ to bulky dye skeletons, and sometimes mixed hydrocarbons, like *n*-octadecane, with dye amphiphiles.³² These methods are indeed effective in improving the monolayer stabilities depending upon circumstances, but are followed by some disadvantages, such as melting point lowering and surface viscosity ascent.

Amphiphiles of $Sh < Sd$, if their hydrophilic properties are strong, can produce monolayers like the hydrochloride of 4. In pertinent literature, group 1a or group 2a compounds, including a strong and/or large hydrophilic group, produced stable monolayers, including for example, TCNQ anions,^{6a,b} pyrene with sulfonium ions,^{7a} merocyanine ions from spiropyran,³³ ruthenium complex ions,³⁴ AQ with two secondary amido groups,^{6b} carbazole with ammonium ions,³⁵ nickel complex ions,³⁶ TTF with two carboxyl groups,^{6d} and porphyrin with four pyridinium ions.³⁷ The alkyl chains of these compounds, however, could not be closely packed together on a water surface.

Molecular Structures and Film Deposition Type. The dialkyl and steroid amphiphiles belonging to groups 3 and 4 generally showed normal Y-type deposition. Both the hydrophobic tails and the dye moieties can be closely packed together on a water surface. Too strong a hydrophilic property, of course, is not good for deposition, which causes expanded film formation and/or peeling off of the deposited film. Amphiphiles belonging to groups 1 and 2 of $Sh < Sd$ often showed YZ- or Z-type deposition.³⁸ This is due to the fact that the hydrophobic groups cannot be packed.

For the large AQ moiety, the steroid skeleton was not sufficiently bulky. Furthermore, we noticed that the LB films of the sterically mismatched amphiphiles were apt to turn to three-dimensional structures on dry substrates.^{39,40} Consequently, the balance in the geometric sizes is important for Y-type deposition.

Monolayer Viscosity and Film Homogeneity. Previous studies by us indicated that monolayers with viscosity values larger than 1 g/s produced solidlike microdomains¹⁵ and generated a wide surface pressure distribution²³ and a large surface pressure drop.²⁴ These were causes for the film inhomogeneity, even when apparent transfer ratios were unity.²⁵ Monolayers with viscosity of about 10^{-2} – 10^{-1} g/s produced soft-type microdomains and did not generate large surface pressure drops, resulting in homogeneous LB films.¹⁵ Lower viscosity values smaller than 10^{-2} g/s, indicated too weak a molecular cohesion to maintain two-dimensional structures on rugged substrates for a long period.^{4,39} These previous results are in accordance with the results obtained in this study. Regardless of the molecular structures including dyes, long alkyl chains, steroid skeletons, and polymers, the existence of the optimum viscosity region for uniform LB films indicates that the film-forming behaviors are not those of molecules, but those of molecular assemblies.

Molecular Structures, Molecular Cohesion, and Monolayer Viscosities. Surface viscosity originates from molecular cohesion of amphiphiles. The enthalpies of melting can be considered to express the molecular cohesion energies in the solid state. According to the enthalpy values, cohesions of the dialkyl derivatives are strong, while those of the steroid derivatives are weak. Cohesions of the monoalkyl derivatives are intermediate between those of the dialkyl and steroid derivatives. Long alkyl chains can be closely packed and show strong van der Waals interaction. The steroid skeletons are rugged and cannot be closely packed. The enthalpy values were in accordance with the surface viscosity measurement results.

Introducing plural long alkyl chains to bulky dye skeletons was effective in improving the monomolecular film stability, but not in decreasing the surface viscosity. The enthalpy values of the compounds, however, decrease by about 1 kcal/mol per carbon atom short. Plural short alkyl chains, such as dodecyl and decyl chains, can be considered both to improve the monolayer stability and to decrease the surface viscosity. This will be related to the fact that some workers succeeded in producing LB films of di- and tridodecyl or decyl dye amphiphiles.^{12,41} On the other hand,

(31) Nakanishi, F.; Shoji, S. *Polym. Prepr. Jpn.* **1987**, *36*, 3254.

(32) (a) Simidzu, T.; Iyoda, T.; Ando, M.; Ohtani, A.; Kaneko, T.; Honda, K. *Thin Solid Films* **1988**, *160*, 67. (b) Sotnikov, P. S.; Berzina, T. S.; Troitsky, V. I.; Valter, R. E.; Karlivan, G. A.; Neiland, O. Ya. *Thin Solid Films* **1989**, *179*, 267.

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(34) Richardson, T.; Roberts, G. G.; Polywka, M. E. C.; Davies, S. G. *Thin Solid Films* **1989**, *179*, 405.

(35) Kimizuka, N.; Tsukamoto, M.; Kunitake, T. *Chem. Lett.* **1989**, 909.

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(37) Raudel-Teixier, A.; Barraud, A.; Belbeoch, B.; Roulliay, M. *Thin Solid Films* **1983**, *99*, 33.

(38) For example, (a) Daniel, M. F.; Lettington, O. C.; Small, S. M. *Thin Solid Films* **1983**, *99*, 61. (b) Nakamura, T.; Matsumoto, M.; Tachibana, H.; Tanaka, M.; Manda, E.; Kawabata, Y. *Thin Solid Films* **1989**, *178*, 413. (c) Richardson, T.; Roberts, G. G.; Polywka, M. E. C.; Davies, S. G. *Thin Solid Films* **1989**, *179*, 405. (d) Facci, J. S.; Falcigno, P. A.; Gold, J. M. *Langmuir* **1986**, *2*, 732. (e) Vincett, P. S.; Barlow, W. A.; Boyle, F. T.; Finney, J. A.; Roberts, G. G. *Thin Solid Films* **1979**, *60*, 265.

(39) Naito, K. *J. Colloid Interface Sci.* **1989**, *131*, 218.

(40) The SEM observation indicated the LB film of the monoalkyl amphiphiles 2 and 24 possessed three-dimensional structures.

(41) (a) Nakamura, T.; Kojima, K.; Matsumoto, M.; Tachibana, H.; Tanaka, M.; Manda, E.; Kawabata, Y. *Chem. Lett.* **1989**, 367. (b) Nakamura, T.; Tanaka, H.; Kojima, K.; Matsumoto, M.; Tachibana, H.; Tanaka, M.; Kawabata, Y. *Thin Solid Films* **1989**, *179*, 183.

such short alkyl chains, however, caused an undesired melting point descent.

In contrast with the plural alkyl chains, the steroid tails could lower the surface viscosities and heighten the melting points. The differences in the melting points between the steroid tails and the plural alkyl chains come from the differences in their entropy terms. The steroid skeletons are rigid and have smaller entropies of melting than the long alkyl chains do. Therefore, the temperature change does not influence the fluidity of the steroid lipid films very much, as shown in Figure 11.

The lowering of the viscosity by the steroid skeleton seems to be in disagreement with the general knowledge that steroids make phospholipid membranes less fluid.⁴² This disagreement is due to the difference in the observed temperatures. In the LB film formation, temperatures below 20 °C are preferable because the long alkyl lipids can form solid films at such low temperatures. In the living cells, the lipids form fluid films, due to higher temperatures and/or unsaturated alkyl chains. The steroid skeletons produce more fluid films in low temperatures, but less fluid films in high temperatures than the long dialkyl chains do.

By introducing the large hydrophilic group (two hydroxy groups) to the PD amphiphiles, the occupied areas were expanded, as shown in Figure 1, and the molecular cohesion was weakened, resulting in the formation of less viscous films. In pertinent literature, *ortho*-dialkyl compounds belonging to group 3b produced rigid films that did not possess good transfer properties.^{26,28} On the other hand, *ortho*-dialkyl amphiphiles with a strong and/or large hydrophilic group belonging to group 3a showed good transfer properties.^{6e,10,27,29,43}

For the TTF moiety, introducing the steroid skeleton was not sufficient to reduce the surface viscosity value. Additional introduction of a large and/or strong hydrophilic group will be necessary.

Molecular Design and Deposition Methods. This paper reports applying the normal vertical dipping method for achieving appropriate transfer properties. Other methods have been proposed for rigid monolayers, such as the horizontal lifting method^{6g,44} and the moving-wall method.⁴⁵ These methods are indeed useful for avoiding the monolayer flow and for decreasing the surface pressure drop. For rather fluid monolayers, these methods have advantages. It was found that the cadmium stearate film (surface viscosity 0.014 g/s at 10 dyn/cm at 18 °C) deposited by the horizontal method was more ordered than that deposited by the vertical method.²⁴ Therefore, producing nonviscous films should be useful, regardless of the deposition methods used.

Conclusion

This study has revealed the relations between the molecular structures of the dye amphiphiles and their film-forming properties. Furthermore, we verified that the amphiphiles, including a steroid hydrophobic tail and/or a large hydrophilic group, yielded good-quality LB films.

For the dye skeletons, (1) stable and condensed monomolecular films were produced if the following geometric relationship was satisfied: $Sh \approx Sd$, where Sh meant a cross-section of the hydrophobic groups and Sd meant a cross-section of the dye; (2) the steroid skeletons raised the melting point of the molecules, while they decreased the molecular cohesion; (3) the steroid skeleton and/or the large hydrophilic group were effective for lowering the molecular cohesion, resulting in the nonviscous monomolecular films and in the uniform LB films.

We have obtained several donor or acceptor amphiphiles, producing uniform monomolecular film without any matrix molecules. Optical and electric properties for LB films including

them will be reported elsewhere.

Experimental Section

Part A. Synthesis. General Procedures. The structures of the products were established by their IR spectra, taken on a Jasco IRA-2 spectrometer, and by ¹H NMR spectra, taken on a Jeol FX90Q NMR spectrometer. Elemental analysis of the products was carried out in Shonan Analysis Center Co. Ltd. The thermal properties of the products were measured on a Du Pont 990 thermal analyzer, using indium metal as a standard. Melting points shown later indicate peak temperatures for the DSC curves. Merck's Kieselgel 60 F₂₅₄ was used for the thin-layer chromatography (TLC).

The synthetic procedure and analytical data of the steroid TCNQ 1 were shown elsewhere.¹⁶ Synthetic details of compounds **9**, **10**, and **18** were shown here. Those of the other compounds were deposited in supplementary material (microfilm edition).

Synthesis of *N*-(Cholestan-3-yl)-*N*-methyl-*p*-phenylenediamine (9**).** Cholestan-3-yl Tosylate (**28**). 5 α -Cholestan-3 β -ol (12.3 g, 31.6 mmol) and tosyl chloride (13 g, 68.2 mmol) were allowed to react in 150 mL of dry pyridine at room temperature for 3 days. The reaction mixture was poured into ice-water containing hydrochloric acid. The resulting precipitate was filtered, dried, and recrystallized from petroleum benzene to give 13.75 g of white crystal (80%). Mp: 137 °C. IR (KBr, cm⁻¹): 2930, 2850 (s, cholestanyl); 1600 (m, Ph); 1460 (m, cholestanyl); 1360, 1180 (m, -SO₂-). ¹H NMR (CDCl₃, ppm): δ 7.79 (d, J = 8.3 Hz, PhH, 2 H); 7.31 (d, J = 8.8 Hz, PhH, 2 H); 4.32 (m, >CHO-, 1 H); 2.44 (s, PhCH₃, 3 H); 2.1–0.6 (cholestanyl, 46 H).

4-(Cholestan-3-ylamino)acetanilide (29**).** **28** (4.69 g, 8.64 mmol) and 4-aminoacetanilide (15 g, 100 mmol) were allowed to react under nitrogen in 80 mL of DMF at 70 °C for 4 h. The reaction mixture was poured into 1000 mL of water to make a precipitate, which was filtered and dried. The precipitate was dissolved in hot toluene and filtered. The filtrate was treated with activated charcoal. The toluene was evaporated under reduced pressure. The residue was dissolved in acetone, into which a small amount of hydrochloric acid was added to make a white precipitate. The precipitate was filtered and stirred vigorously with toluene/sodium hydroxide aqueous solution. The toluene was evaporated under reduced pressure. The resulting residue was recrystallized from the petroleum benzene to give 0.92 g of white solid (20%). Mp: 193 °C. IR (KBr, cm⁻¹): 2930, 2850 (s, cholestanyl); 1660 (m, C=O); 1605 (m, -NH-); 1520 (m, Ph); 1470 (m, cholestanyl). ¹H NMR (DMSO *d*₆, ppm): δ 9.44 (s, -NHCO-, 1 H); 7.21 (d, J = 8.6 Hz, PhH, 2 H); 6.50 (d, J = 8.5 Hz, PhH, 2 H); 5.25 (br, -NH-, 1 H); 3.5 (br, >CHN-, masked by H₂O); 1.95 (s, COCH₃, 3 H); 1.8–0.6 (cholestanyl, 46 H). Anal. Calcd. for C₃₅H₅₆N₂O: C, 80.71; H, 10.84; N, 5.38. Found: C, 81.12; H, 10.94; N, 5.45.

(4-Acetamidophenyl)cholestan-3-ylmethylammonium Iodide (30**).** **29** (0.53 g, 1.0 mmol) and methyl iodide (10 mL, 160 mmol) were allowed to react in 40 mL of toluene under nitrogen at 60 °C for 11 h. A precipitate was obtained after the mixture stood at room temperature overnight. The precipitate was filtered and dried to produce 0.62 g of white solid (92%). Mp: 204 °C. IR (KBr, cm⁻¹): 2930, 2850 (s, cholestanyl); 1690 (s, C=O); 1615 (m, -NH-); 1520 (m, Ph); 1450 (m, cholestanyl). ¹H NMR (CDCl₃, ppm): δ 9.38 (br, NH⁺, 1 H); 8.00 (d, J = 8.4 Hz, PhH, 2 H); 7.82 (d, J = 8.5 Hz, PhH, 2 H); 3.8 (br, >CHN, 1 H); 3.26 (br, -NCH₃, 3 H); 2.0–0.6 (cholestanyl, 46 H). Anal. Calcd. for C₃₆H₅₉N₂O: C, 65.24; H, 8.97; N, 4.23; I, 19.15. Found: C, 65.35; H, 8.96; N, 4.30; I, 18.70.

***N*-(Cholestan-3-yl)-*N*-methyl-*p*-phenylenediamine (**9**).** The ethanol solution containing **30** (0.42 g, 0.63 mmol) and 3 mL of hydrochloric acid was refluxed for 14 h. The ethanol was evaporated under reduced pressure. The residue was washed with acetone and then stirred vigorously in toluene/sodium hydroxide aqueous solution under nitrogen. The toluene solution was separated, washed with water, and then dried over magnesium sulfate. The toluene was evaporated under reduced pressure. The residue was recrystallized from the methanol/toluene solution, resulting in 0.13 g of white solid (42%). Mp: 116 °C. IR (KBr, cm⁻¹): 2930, 2850 (s, cholestanyl); 1515 (m, Ph); 1462 (m, cholestanyl). IR (Nujol, cm⁻¹): 3340, 3200 (w, -NH₂); 1610 (m, -NH₂). ¹H NMR (CDCl₃, ppm): δ 7.12 (d, J = 8.5 Hz, PhH, 2 H); 6.79 (d, J = 8.5 Hz, PhH, 2 H); 3.00 (br, >CHN, 1 H); 2.60 (s, NCH₃, 3 H); 2.9–0.6 (cholestanyl, 46 H). TLC (ethyl acetate): R_f = 0.76. Anal. Calcd. for C₃₄H₅₆N₂: C, 82.86; H, 11.45; N, 5.68. Found: C, 82.66; H, 11.91; N, 5.73.

Synthesis of *N*-(Cholestan-3-yl)-*N*-methyl-*N'*,*N'*-bis(2-hydroxyethyl)-*p*-phenylenediamine (10**).** The dihydrochloride of **9** (2.09 g, 3.69 mmol), 2-bromoethanol (3.0 g, 24 mmol), and sodium hydrogen carbonate (2.0 g, 24 mmol) were allowed to react under nitrogen in 50 mL of DMF at 100 °C for 10 h. The reaction mixture was poured into 1000 mL of sodium chloride aqueous solution to yield a precipitate. The

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precipitate was dissolved in acetone, into which hydrochloric acid was added to make a white precipitate. The precipitate was filtered and dried to give 2.05 g of white powder. A 1.0-g portion of the powder was stirred vigorously in ether/sodium hydroxide aqueous solution. The ether was evaporated under reduced pressure. The residue was recrystallized from the petroleum benzene, resulting in 0.2 g of white solid (19%). Mp: 172 °C. IR (KBr, cm^{-1}): 2930, 2850 (s, cholestanyl); 1520 (s, Ph); 1460 (m, cholestanyl); 1360, 1065 (m, $-\text{CH}_2\text{OH}$). ^1H NMR (CDCl_3 , ppm): δ 7.00 (s, PhH, 2 H); 6.68 (br, PhH, 2 H); 3.81, 3.53 (br, $-\text{CH}_2\text{CH}_2\text{OH}$, 10 H); 3.1 (br, $>\text{CHN}$, 1 H); 2.6 (br, NCH_3 , 3 H); 2.0–0.6 (cholestanyl, 46 H). TLC (ethyl acetate): R_f = 0.71. Anal. Calcd. for $\text{C}_{38}\text{H}_{64}\text{N}_2\text{O}_2$: C, 78.57; H, 11.10; N, 4.82. Found: C, 78.79; H, 10.86; N, 4.82.

Synthesis of *N*-(2-Octadecyleicosanesulfonyl)-*N'*-methanesulfonyl-*p*-quinonedilimine (18). (2-Octadecyleicosyl)isothiuronium Tosylate (31). The 2-propanol solution (150 mL) containing 2-octadecyleicosyl tosylate (5.1 g, 7.2 mmol; mp 58 °C; prepared from 2-octadecyleicosanoic acid⁴⁶) and thiourea (5.6 g, 73 mmol) was refluxed for 20 h. A 50-mL portion of water was added to the reaction mixture to make a precipitate, which was filtered and washed with water. A yield 5.36 g of white powder was obtained (95%). Mp: 79 °C. IR (KBr, cm^{-1}): 2920, 2850 (s, alkyl); 1210, 1170, 1130, 1030. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ 8.92 (br, NH_2 , 4 H); 7.50 (d, J = 8.1 Hz, PhH, 2 H); 7.09 (d, J = 8.3 Hz, PhH, 2 H); 3.08 (SO_2CH_2 , masked with water); 2.29 (s, PhCH_3 , 3 H); 2.5–1.0 ($-(\text{CH}_2)_{17}-$, $>\text{CH}-$, 69 H); 0.85 (t, $-\text{CH}_3$, 6 H). Anal. Calcd. for $\text{C}_{46}\text{H}_{88}\text{N}_2\text{O}_3\text{S}_2$: C, 70.71; H, 11.35; N, 3.59. Found: C, 70.93; H, 11.70; N, 3.24.

***N*-(2-Octadecyleicosanesulfonyl)-*N'*-methanesulfonyl-*p*-phenylenediamide (32).** 31 (1.0 g, 1.3 mmol) and bromine (2.6 g, 16 mmol) were allowed to react in 100 mL of cooled water below 10 °C for 4 h. Into the reaction mixture, 200 mL of cooled dichloromethane was added, and then sodium sulfite was gradually added to make the red color disappear. The dichloromethane solution was dried over calcium chloride and then evaporated. The residue was dissolved in 40 mL of dry pyridine, into which 4-aminomethanesulfonyl anilide (0.94 g, 5 mmol) was added. The reaction mixture was stirred at room temperature for 6 h, and then poured into 500 mL of diluted hydrochloric acid to make a precipitate. The precipitate was washed with methanol and with petroleum benzene, and recrystallized from the ethanol solution to give 0.19 g of white powder (19%). Mp: 120 °C. IR (KBr, cm^{-1}): 3280 (s, NH); 2920, 2850 (s, alkyl); 1520 (s, Ph); 1470 (s, alkyl); 1320, 1140 (vs, $-\text{SO}_2-$). ^1H NMR (CDCl_3 , ppm): δ 7.21 (s, PhH, 4 H); 6.68 (s, NH, 2 H); 3.30 (s, SO_2CH_3 , SO_2CH_2 , 5 H); 2.5–1.0 ($-(\text{CH}_2)_{17}-$, $>\text{CH}-$, 69 H); 0.88 (t, $-\text{CH}_3$, 6 H). Anal. Calcd. for $\text{C}_{45}\text{H}_{86}\text{N}_2\text{O}_4\text{S}_2$: C, 69.00; H, 11.07; N, 3.58; S, 8.19. Found: C, 68.70; H, 10.85; N, 3.53; S, 7.98.

***N*-(2-Octadecyleicosanesulfonyl)-*N'*-methanesulfonyl-*p*-quinonedilimine (18).** The dry acetic acid solution (40 mL) containing 32 (0.15 g, 0.19 mmol) and lead tetraacetate (0.15 g, 0.80 mmol) was heated at 70 °C for 6 h. The reaction mixture was allowed to stand overnight at room temperature to yield a precipitate. The precipitate was filtered and washed with acetic acid and with acetonitrile, and then recrystallized from the acetic acid solution to yield 0.14 g of yellow powder (94%). Mp: 76 °C. IR (KBr, cm^{-1}): 2920, 2850 (s, alkyl); 1580, 1570 (s, $\text{C}=\text{C}$, $\text{C}=\text{N}$); 1470 (m, alkyl); 1320, 1300, 1140 (s, $-\text{SO}_2-$). ^1H NMR (CDCl_3 , ppm): δ 7.96, 7.86 ($\text{CH}=\text{}$, 2 H); 6.94, 6.82 ($\text{CH}=\text{}$, 2 H); 3.26 (s, SO_2CH_3 , SO_2CH_2 , 5 H); 2.5–1.0 ($-(\text{CH}_2)_{17}-$, $>\text{CH}-$, 69 H); 0.88 (t, $-\text{CH}_3$, 6 H). TLC (chloroform): R_f = 0.69. Anal. Calcd. for $\text{C}_{45}\text{H}_{84}\text{N}_2\text{O}_4\text{S}_2$: C, 69.18; H, 10.84; N, 3.59. Found: C, 68.99; H, 10.63; N, 3.66.

Part B. Measurements of Monomolecular Film Properties. Apparatus. A Joyce-Loebl Langmuir trough 4 was modified to include a dipping system containing a stepping motor, a temperature regulator, and two moving teflon bars instead of the teflon belt. The other parts of the equipment, for example, a Wilhelmy surface balance with filter paper, were not modified.

Deposition Procedure. Measurement of π - A curves and formation of the LB films were carried out by the ordinary methods. Typical conditions were as follows: subphase, pure water freshly deionized by ion-exchange resins; temperature, subphase at 18 °C, atmosphere at 20–22 °C; concentration and volume of the amphiphile toluene solution poured onto the subphase, 0.5 mmol/L, 100 μL ; initial area, 350 cm^2 ; compression speed, 5 cm^2/min ; deposition surface pressure, 25 dyn/cm ; deposition speed, 5 mm/min . The substrate was treated in the following way: Single-crystal silicon substrates, which had mirror surfaces on both sides, were treated with a diluted hydrofluoric acid and with a mixture of concentrated sulfuric acid and hydrogen peroxide water (3/1 v/v), and washed with water. After baking the substrates, a silane coupling agent (hexamethyldisilazane) was allowed to react with the substrates, to make their surfaces hydrophobic.

Measurements of surface viscosity and surface pressure drop were described in a previous paper.¹⁵

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Supplementary Material Available: Synthetic details and analytical data of compounds 3–8, 11–17, and 19–27 (15 pages). Ordering information is given on any current masthead page.

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