

Adsorbed Monolayers of a 1,1,1-Trimethylaminimide with Azobenzene Unit

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A 1,1,1-trimethylaminimide having an azobenzene unit was prepared to study adsorption behavior, taking notice of the betaine structure as a polar head, and *E*-to-*Z* photoisomerization of its adsorbed monolayers. The corresponding carboxylic acid and 1,1-dimethylhydrazide were also synthesized to make comparative study with the aminimide.

Key word: Adsorption, Monolayer, Aminimide, Interface, Azobenzene.

1. INTRODUCTION

Since the nature and structures of solid surfaces determine crucially chemical as well as physical properties of materials participating in various interfacial phenomena, surface modification of solid materials has attracted interest from fundamental and practical viewpoints [1]. Organic ultra-thin films such as self-assembled monolayers (SAMs) generated by the adsorption of organic molecules onto solid surfaces have been extensively used to modify surface properties of underlying substrates. We reported preparative methods for SAMs on silica substrates through hydrogen bonds using some amphiphiles to fabricate photoactive surfaces [2] and revealed that the stability of SAMs assembled through noncovalent bonds is enhanced by multi-point adsorptivity, whereas desorption resistance is also improved by additional effect of ion pairing interaction between cationic adsorbate and an outermost substrate surface [3].

In this work, an aminimide moiety was chosen as a polar head group of an adsorbate to form SAMs on silica substrates. Due to their characteristic zwitter ionic structure resulting in electrostatic interactions toward polar substrate surfaces, enhancement of adsorption efficiency will be expected. Designed structures of molecules used in this study are shown in Figure 1. An azobenzene chromophore was introduced to these structures as a probe to monitor ordering and environmental effect on molecular assembly in adsorbed films.

2. EXPERIMENTAL

2.1. Materials

All organic reagents were purchased from Tokyo Kasei Kogyo and used as received.

1,1,1-Trimethylhydrazinium iodide (1)

To a solution of 1,1-dimethylhydrazine (3.00 g, 50.0 mmol) in ethanol (50 ml), a solution of methyl iodide (7.45 g, 50 mmol) in ethanol (20 ml) was added. The resulting solution was stirred for 5 h at room temperature, and the solvent was evaporated under reduced pressure. A residue was recrystallized from methanol to give 10.0 g

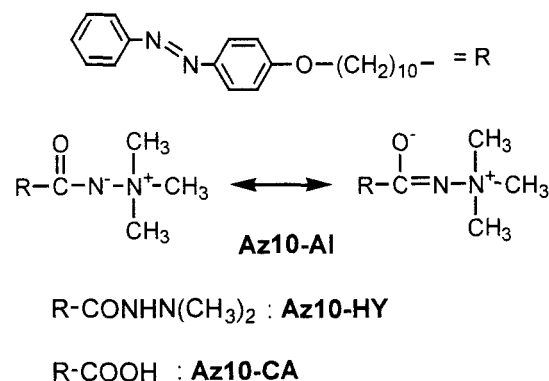


Fig. 1. Molecular structures of materials used in this study.

(95 % yield) of pure **1** as a white solid. ¹H-NMR (200 MHz, CDCl₃) δ (ppm): 3.26 (2H, s, -NH₂), 3.34 (9H, s, -N⁺(CH₃)₃). Anal Calcd for C₃H₁₁N₂I: C, 5.49; H, 17.84; N, 13.86; I, 62.81 %. Found: C, 5.15; H, 17.92; N, 14.00; I, 63.37 %.

Ethyl 11-[4-(phenylazo)phenoxy]undecanoate (2)

To a solution of 4-hydroxyazobenzene (10.0 g, 50.5 mmol) and ethyl 11-bromoundecanoate (16.2 g, 55.5 mmol) in dry acetone (150 ml) was added potassium carbonate (17.4 g, 125 mmol) and a catalytic amount of potassium iodide, and the mixture was heated under reflux for 5 h. The reaction mixture was poured into water (500 ml) and extracted with ether (100 ml × 3). A combined organic layer was washed with water, dried over anhydrous magnesium sulfate and evaporated to dryness. The residue was recrystallized from hexane to give 15.1 g (73 % yield) of **2** as yellow crystals of mp 75-76 °C. ¹H-NMR (200 MHz, CDCl₃) δ (ppm): 1.20-1.70 (17H, m, -(CH₂)₇-, -CH₃), 1.75-1.89 (2H, m, -CH₂-), 2.29 (2H, t, J = 7.3 Hz, -CH₂-CO-), 4.04 (2H, t, J = 6.7 Hz, -Ar-O-CH₂-), 4.14 (2H, q, J = 5.0 Hz, -O-CH₂-), 6.95-7.05 (2H, m, Ar-H₂), 7.41-7.58 (3H, m, Ar-H₃), 7.82-7.95 (4H, m, Ar-H₂).

1,1,1-Trimethylamine[11-(4-(phenylazo)phenoxy)undecanoylimide (Az10-AI)

A solution of **1** (1.04 g, 5.2 mmol), **2** (2.00 g, 4.9 mmol) and (60 %) sodium hydride (0.24 g, 6.2 mmol) in dry DMSO (40 ml) was stirred for 20 h at room temperature. The reaction mixture was poured into ice water (200 ml), stirred for 30 min and extracted with chloroform. An organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from a 6:4 (v/v) mixture of THF and hexane to give 1.37 g (65 % yield) of Az10AI as a yellow solid of mp 78-80 °C. ¹H-NMR (200 MHz, CDCl₃) δ (ppm): 1.27-1.40 (8H, m, -(CH₂)₄-), 1.40-1.53 (2H, m, -CH₂-), 1.54-1.67 (2H, m, -CH₂-), 1.67-1.75 (2H, m, -CH₂-), 1.75-1.87 (2H, m, -CH₂-), 2.03 (2H, t, J = 7.6 Hz, -CH₂-CO-), 3.37 (9H, s, -N⁺(CH₃)₃), 4.03 (2H, t, J = 6.6 Hz, -O-CH₂-), 6.98-7.04 (2H, m, Ar-H₂), 7.38-7.54 (3H, m, Ar-H₃), 7.85-7.94 (4H, m, Ar-H₂). Anal Calcd for C₂₆H₃₈N₄O₂·0.5H₂O: C, 69.77; H, 8.78; N, 12.52 %. Found: C, 69.34; H, 8.99; N, 12.33 %. ε_{346 nm} = 2.6 × 10⁵ (dm³ mol⁻¹ cm⁻¹).

11-[4-(Phenylazo)phenoxy]undecanoic acid (Az10-CA)

A solution of **2** (5.00 g, 122 mmol) in THF (100 ml) was mixed with 2N-HCl (60 ml), stirred for 1 h at room temperature and extracted with chloroform (100 ml × 2). The organic layer was washed with a saturated NaCl aqueous solution, dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give a residue, which was recrystallized from a 1:9 (v/v) mixture of THF and hexane to give 4.51 g (92 % yield) of Az10-CA as a yellow solid of mp 128-130 °C. ¹H-NMR (200 MHz, CDCl₃) δ (ppm): 1.22-1.71 (14H, m, -(CH₂)₇-), 1.74-1.91 (2H, m, -CH₂-), 2.35 (2H, t, J = 5.0 Hz, -CH₂-CO-), 4.04 (2H, t, J = 4.3 Hz, -O-CH₂-), 6.96-7.06 (2H, m, Ar-H₂), 7.42-7.56 (3H, m, Ar-H₃), 7.84-7.95 (4H, m, Ar-H₂). ε_{346 nm} = 2.4 × 10⁵ (dm³ mol⁻¹ cm⁻¹).

1,1-Dimethyl-2-[11-(4-(phenylazo)phenoxy)undecanoyl]hydrazide (Az10-HY)

A mixture of Az10-CA (1.50 g, 4.1 mmol) and thionyl chloride (2.00 g, 10.0 mmol) in dry toluene (30 ml) was stirred for 1 h at 70 °C. The solvent was evaporated to dryness. Subsequently, a solution of 1,1-dimethylhydrazine (0.30 g, 4.1 mmol) and triethylamine (0.83 g, 8.2 mmol) in dry toluene (20 ml) was added and refluxed for 1 h. The reaction mixture was poured into diethyl ether (50 ml) and filtered to remove triethylamine hydrochloride. The solution was washed with water and a saturated NaCl aqueous solution, dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from a 3:7 (v/v) mixture of THF and hexane to give 1.05 g (63 % yield) of Az10-HY as a yellow solid of mp 109-111 °C. ¹H-NMR (200 MHz, CDCl₃) δ (ppm) 1.27-1.40(8H, m, -(CH₂)₄-), 1.40-1.53 (2H, m, -CH₂-), 1.54-1.67 (2H, m, -CH₂-), 1.67-1.75 (2H, m, -CH₂-), 1.75-1.87 (2H, m, -CH₂-), 2.03 (2H, t, J = 7.6 Hz, -CH₂-CO-), 2.55 (6H, d, -N(CH₃)₂), 4.03 (2H, t, J = 6.6 Hz, -O-CH₂-), 6.98-7.04 (2H, m, Ar-H₂), 7.38-7.54 (3H, m, Ar-H₃), 7.85-7.94 (4H, m, Ar-H₂). ε_{346 nm} = 2.3 × 10⁵ (dm³ mol⁻¹ cm⁻¹).

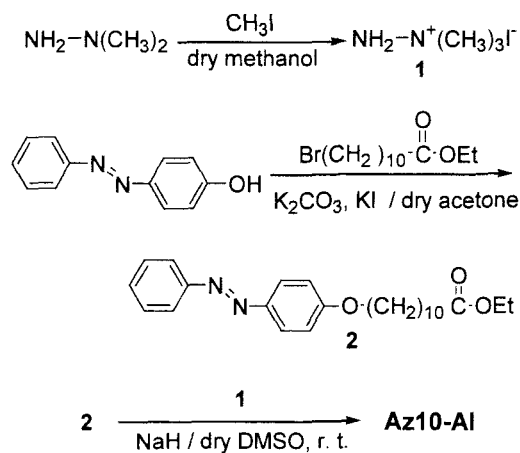


Fig. 2. Synthetic pathway to Az10-AI.

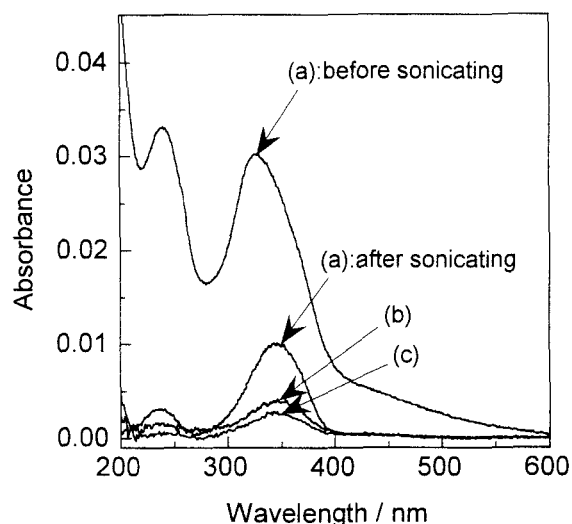


Fig. 3. UV-Visible absorption spectra of adsorbed (a) Az10-AI before and after ultrasonical treatment and (b) Az10-HY and (c) Az10-CA with no ultrasonical treatment.

2.2. Sample preparation

Quartz plates (10 × 30 × 1 mm) were immersed overnight in a saturated sodium hydroxide solution in ethanol, washed thoroughly with pure water (Milli-Q), acetone and toluene. Subsequently, the plates were immersed in a toluene solution of an adsorbate (conc. 1 × 10⁻⁴ mol dm⁻³) for various minutes at 25 °C, rinsed with toluene, sonicated in hexane for 20 min and finally dried at 60 °C for 30 min in an oven.

2.3. Measurements

Melting points were measured with a Yanaco MP-S3S melting-point apparatus. ¹H-NMR spectra were taken with a Bruker AC-200 spectrometer using tetramethylsilane (Merck) as an internal standard. Elemental analysis was performed on a Yanaco MT-5 CHN CORDER. FT-IR spectra were recorded on a Fourier transform infrared spectrometer (Bio Rad,

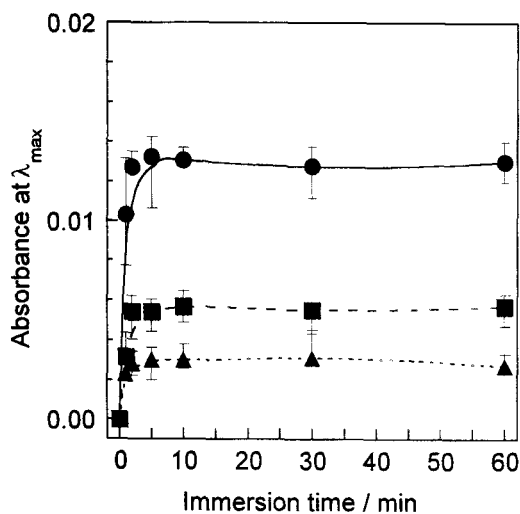


Fig. 4. Absorbance changes of adsorbed monolayers on silica substrates during immersion in toluene (25 °C): Az10-AI (●), Az10-HY (■) and Az10-CA (▲).

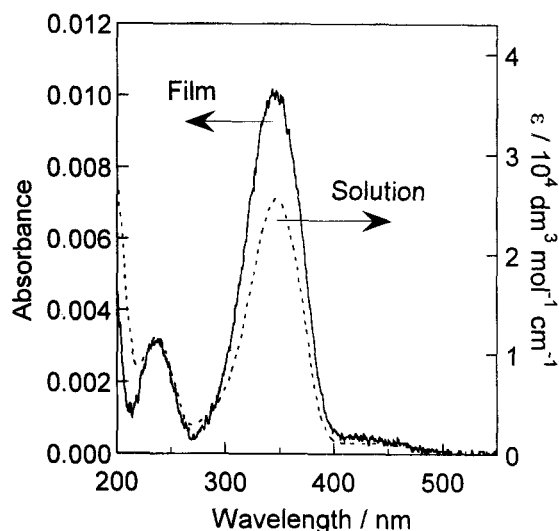


Fig. 5. UV-Visible absorption spectra of Az10-AI in acetonitrile (----) and in an adsorbed monolayer after sonicating for 20 min (—).

FTS-6000), whereas KBr pellets were prepared for transmission spectra. Absorption spectra of adsorbed films were measured using a JASCO MAC-1 type weak absorption spectrometer. Absorption spectra of solutions were taken with a diode-array spectrometer (Hewlett Packard HP8452A). Solvents used for spectroscopic measurements were of a spectroscopic grade (Uvasol, Cica-Merck). Photoisomerization of the materials was achieved by irradiation with 365 nm line from a 150 W Hg-Xe lamp (San-ei UV Supercure-230S) passed through UV-35 and UV-D36A filters (Toshiba). Light intensity was monitored by an optical power meter (Advantest TQ-8210).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Structural Elucidation

Trialkylamine-acylimide derivatives have been synthesized by two synthetic routes starting from 1,1-dimethylhydrazin. Hinmann [4] and Wawzonek [5] et al. reported the preparative method of aminimides derived from tertiary aliphatic amine from hydrazides, which are quaternized to hydrazinium halides, followed by treatment with alkaline to form the corresponding aminimides. Berry [6] and Kameyama [7, 8] et al. obtained trialkylamine-acylimides by the acylation of 1-alkyl-1,1-dimethylhydrazinium halides with acid chloride, followed by alkaline treatment. These methods involve three steps. On the other hand, the key compound in this study, Az10-AI, was prepared conveniently by the reaction of the corresponding ester with a 1,1,1-trimethylhydrazinium halide in the presence of an anhydrous base according to the method reported by McKillip [9] et al. with a slight modification (Figure 2). The employment of sodium hydride [10] as a base suspended in dimethylsulfoxide gave moderate reaction conditions and a high yield because of strong nucleophilicity of the intermediate, 1,1,1-trimethylaminimide, as reported by McKillip [9].

The structure of Az10-AI was confirmed by NMR, IR spectra and elemental analysis. It is known that acylaminimides show a very strong IR absorption band at around 1700 cm^{-1} due to the stretching frequency of $\text{OC}=\text{N}$ bond in the resonance form [11]. Since the carbonyl frequency in the protonated form of the aminimide around 1700 cm^{-1} is completely suppressed, this resonance form makes a major contribution to the actual structure. Az10-AI possesses the IR absorption band at 1576 cm^{-1} , suggesting that the aminimide moiety of Az10-AI displays the delocalization of the electron pair in the p-orbital of the imide nitrogen with the p-orbital of the carbonyl to cause the coplanarity of the OCNN system as reported in a literature [11].

3.2. Adsorption on silica plates

Adsorption of the three amphiphilic azobenzenes was examined by immersing fused silica plates in their toluene solutions, followed by rinsing in toluene. As shown in Figure 3, the π,π^* -absorbance of Az10-AI on the plate is about 0.03 and too large for monolayered azobenzene, taking the absorption coefficient of the chromophore into consideration. The π,π^* -absorption band suffers from slight blue shift, indicating the formation of H-aggregates, whereas the deformed baseline of the spectrum is indicative of light scattering owing to the formation of aggregations. These results indicate strongly that the adsorbed film of the aminimide is not of a monolayer, but rather a multilayered structuring. It followed that the plate was subjected to ultrasonical treatment to result in a gradual reduction of the absorbance, which was leveled off after 10 min. Note that the π,π^* -absorption band is equivalent of that in solution, indicating that no aggregation form exists in the adsorbed monolayer. These facts imply that the ultrasonical treatment is an effective way to give rise to a monolayered structure (Figure 3). An occupied area of

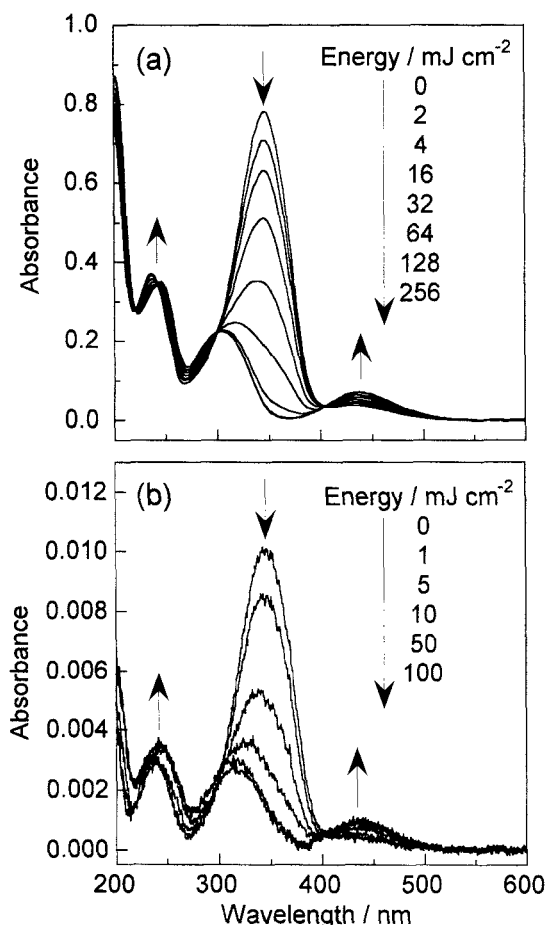


Fig. 6. UV-Visible absorption spectral changes of Az10-AI (a) in acetonitrile and (b) in the adsorbed monolayer upon irradiation with 365 nm light.

Az10-AI of the monolayer was estimated to be $1.2 \text{ nm}^2 \text{ molecule}^{-1}$ on the basis of the absorption spectrum.

It was reported that π -A isotherm measurements of aminimides with long alkyl chains show a surface pressures rise at around $0.8 \text{ nm}^2 \text{ molecules}^{-1}$ [12]. This value is not much far from the occupied area of the adsorbed Az10-AI, implying that the surface adsorption technique provides a convenient procedure to cover a silica surface with a monolayer of Az10-AI exhibiting a relatively dense packing. Thorough desorption of Az10-AI occurred when the plate was rinsed with ethanol, indicating that Az10-AI adsorbs on the surface through hydrogen bonding and electrostatic interaction.

Figure 4 shows absorption behavior of the three adsorbates in toluene at 25°C . The absorptivity is in the following order; Az10-AI \gg Az10-HY $>$ Az10-CA. The enhanced adsorption of Az10-AI, when compared with Az10-CA and Az10-HY, supports the involvement of electrostatic interactions of the betaine structure in addition to the effect of hydrogen bonding.

UV-visible absorption spectra of Az10-AI in an adsorbed monolayer and in an acetonitrile solution are shown in Figure 5. It is worthy to stress here that the π - π^* absorption band is not far from each other, indicating that molecular interactions among the azobenzene moieties are not included in the adsorbed film. Figure 6 shows absorption spectral changes of Az10-AI in acetonitrile and on a silica plate upon irradiation with 365 nm light, respectively. The azobenzene in the monolayer exhibits high *E*-to-*Z* photoisomerizability of 89.6 %, indicating that a sufficient free volume in the adsorbed monolayer is ensured for *E*-to-*Z* photoisomerization.

4. CONCLUSION

The aminimide bearing azobenzene chromophore, Az10-AI showed better adsorptivity on a silica surface from a dilute solution of less polar solvents when compared with the corresponding hydrazide and carboxylic acid. The enhancement of adsorptivity comes not only from hydrogen bonding, but also from electrostatic interactions between the zwitter ionic polar head and a silica surface.

We thank Prof. T. Seki, Dr. S. Morino, Dr. M. Nakagawa and Dr. K. Arimitsu in our laboratory for technical assistance and helpful discussions.

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(Received December 7, 2000; Accepted March 23, 2001)