Amino Acids (1996) 10: 333–343

Amino
Acids

Photoactive amino acid derivatives with long alkyl chains

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Accepted December 6, 1995

Summary. Azobenzene amphiphiles containing β-alanine, L-lysine or β-homolysine moieties were synthesized and characterised. Stable monomolecular layers at the air/water interface and LB multilayers has been obtained from some of them. One sample of azobenzenes synthesized has been shown to undergo a reversible trans/cis photoisomerization upon light irradiation in both solution and LB multilayer.

Keywords: Amino acids – β-Alanine – L-Lysine – β – Homolysine – Azobenzene – Photoisomerization – Monomolecular layer – Multilayer

Abbreviations: DCC – N,N′-dicyclohexyl carbodiimide, HONSu – N-hydroxy succinimide, Boc – t-butyloxycarbonyl, Bu^t – t-butyl, EtOAc – ethyl acetate, THF – tetrahydrofuran, TEA – triethylamine, HPLC – high performance liquid chromatography, TLC-thin layer chromatography, Ph – phenyl, i-PrOH – isopropyl alcohol.

Introduction

Our major target has been to synthesize a series of α- and β-amino acid derivatives, containing photoactive azobenzene moiety and long alkyl chains, for photoresponsive organized materials in mono-, bi- and multilayers.

Much attention has been attracted by photoresponsive polypeptides containing azobenzene moiety (Yamamoto, 1990; Menzel, 1993).

Synthesis and reversible solubility change by trans/cis photoisomerization of N^2,N^6-di(4-phenylazobenzoyl)-lysine has been reported by Yamamoto (1988). A number of lysine and ornithine amphiphiles bearing one or two amide groups along the chain has been proposed for polar Z-type Langmuir – Blodgett films by Popovitz-Biro (1990). As to our knowledge, amphiphilic β-alanine derivatives bearing azobenzene moiety are not known.

Material and methods

All solvents were reagent grade and distilled before use. N,N′-dicyclohexyl carbodiimide, N,N-diisopropylethyl amine, N-hydroxy succinimide and β-alanine were used as received from Aldrich.

Melting points reported were detected on Boetius apparatus. NMR spectra were taken on a Brucker WH 90/DS spectrometer, using tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer 580 B spectrometer, a Nujol mull technique was employed. Electronic absorption spectra were recorded on a Specord UV-VIS spectrometer for $CHCl_3$ solutions. HPLC analysis was performed on a Du Pont (8800) apparatus with UV detector. The conditions for the analyses were as follows: column Silasorb SPH 600, 4.6 × 250 mm, eluents for **2** i-PrOH-heptane 40:60, for **3** i-PrOH-AcOH-hexane 30:1:69, for **4** i-PrOH-heptane 10:90, for **8** i-PrOH-AcOH-heptane 20:1:79, for **9** i-PrOH-AcOH-heptane 20:1:79 v/v were used. The detection wavelength was 254 nm. TLC was carried out on Silufol with the following solvent systems: $CHCl_3$-EtOAc 3:1 (A), hexane-EtOAc 1:5 (B), $CHCl_3$-EtOAc 1:4 (C), hexane-EtOAc 1:1 (D), $CHCl_3$-EtOAc 1:2 (E), $CHCl_3$-EtOAc 17:3 (F), benzene-EtOAc 1:1 (G), n-BuOH-AcOH-H_2O 4:1:5 (H), benzene-EtOAc 1:2 (I). After being sprayed with phosphomolybdic acid, plates were heated at 120°C for 5 min. Optical rotation was measured using Autopol II (Rudolph Research, USA) polarimeter.

Photoisomerization in solutions and in LB multilayers

Solutions of compounds **2**, **3**, **8** and **9** in $CHCl_3$ with the concentration 2×10^{-4}–2.4×10^{-4} M were irradiated from a high pressure mercury lamp (SVD-120A) using the filter centered at 360 nm. The solution of **4** and LB films of **3**, **4** were irradiated from Xenon lamp DKS-L-250i using the filter centered at 360 nm or interference filter at 452 nm.

Monomolecular layer experiments

π-A Isotherms were obtained on the computer-controlled Langmuir trough by "step by step" method (Markava, 1992). The spreading solutions in $CHCl_3$ were freshly prepared and stored in a dark box. Concentration was in range from 1.9×10^{-3} to 2.40×10^{-3} M. All investigations were made at ambient temperature (18–20°C). As subphase double distilled water (pH 5.8) was used.

Multilayer experiments

The LB multilayers were deposited onto hydrophilic (**2**, **3**) or hydrophobic (**4**) quartz substrates at the pressure 25 mN/m (**2**, **3**) or 14 mN/m (**4**) with deposition speeds 7.5 mm/min (**2**, **3**) and 30 mm/min downwards and 7.5 mm/min upwards (**4**). The substrates were cleaned and rendered hydrophilic by first immersing them in $K_2Cr_2O_7$ (about 5 weight %) solution in concentrated H_2SO_4 for 12 h and subsequently soaking in 50% H_2SO_4 for 40 min., followed by thoroughly rinsing with double distilled water, acetone, $CHCl_3$. The cleaned substrates were hydrophobized by immersing in dimethyldichlorsilane:hexane, volume ratio 1:20 for 50 min., then washed with hexane, acetone, hexane.

*General procedure for the preparation of β-alanine derivative **3** and L-lysine derivative **9***

DCC (2.42 mmol) was added to a stirred solution of **1** (1.92 mmol) in THF (50 mL) while keeping the temperature below 3°C. After additional 5 min HONSu (2.52 mmol) was

added, then stirring was continued for 5 h at room temperature. The reaction mixture was filtered, and the solution of β-alanine (1.9 mmol) in water (30 mL) was added dropwise, then TEA was added to pH 9–10. After 24 h the reaction mixture was acidified with 6 N HCl to pH 2, diluted with water (150 mL), then extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, evaporated. The residue was purified on a Silicagel L 40/100 column. The reaction was controlled by TLC on Silufol, solvent system A.

*4-[4-(Methyl-palmitoyl-amino)phenyl-azo]benzoyl-β-alanine (**3**)*

Eluent for column chromatography A, yield 45%, m.p. 158–159°C, purity established by HPLC 98.9%, R_f(B) 0.68, R_f(C) 0.55. ^{1}H NMR (DMSO-d_6, ppm.: 0,84 (3 H, CH_3), 1.18 (26 H, CH_2), 2.16 (2 H, CH_2CO), 2.6 (2 H, CH_2COOH), 3.27 (3 H, NCH_3), 3.48 (2 H, CH_2N), 7.53 (2 H, Ph), 7,89 (2 H, Ph), 7.94 (2 H, Ph), 8.04 (2 H, Ph), 8.68 (1 H, NHCO), 12.18 (1 H, COOH). IR (cm^{-1}): 3,365, 1,711, 1,648, 1,552. UV, λ_{max}: 341 nm (ε 25,300), 454 nm (ε 830).

*N^2-Boc-N^6-4-[4-(Methyl-palmitoylamino)phenylazo]benzoyl-L-lysine (**9**)*

As for amine component N^2-Boc-L-lysine was used, eluent for column chromatography was D, yield 62%, m.p. 53–54°C, purity established by HPLC 99.1%, R_f(D) 0.19, R_f(E) 0.34. ^{1}H NMR(DMSO-d_6), ppm.: 0.85 (3 H, CH_3), 1.18 (26 H, CH_2), 1.39 (9 H, Bu^t), 2.17 (2 H, CH_2CO), 3.84 (1 H, CH), 7.03 (1 H, NHBoc), 7.6 (2 H, Ph), 7.95 (2 H, Ph), 8.04 (2 H, Ph), 8.13 (2 H, Ph), 8.63 (1 H, NHCO). IR (cm^{-1}): 3,433, 3,328, 1,723, 1,688, 1,540, 1,523. UV, λ_{max}: 342 nm (ε 25,800), 453 nm (ε 320), $[\alpha]_D^{22} = +3$ (THF, c = 1.5).

*N,N′-Dicyclohexyl-N-4-[4-(methyl-palmitoylamino)phenylazo]benzoyl-urea (**4**)*

DCC (0.14 g, 0.68 mmol) was added to a stirred solution of **1** (0.24 g, 0.49 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 3 h, then filtered and evaporated. The residue was purified on Silicagel L 100/160 column with eluent F. Yield 0.24 g (71%) of **4**, m.p. 118–119°C, purity established by HPLC 99.4%, R_f(F) 0.76. ^{1}H NMR (DMSO-D_6), ppm.: 0.84 (3 H, CH_3), 1.18 (26 H, CH_2), 1.38 (20 H, C_6H_{11}), 2.07 (2 H, CH_2CO), 3.3 (3 H, CH_3N), 7.53 (2 H, Ph), 7.73 (1 H, NH), 7,84 (2 H, Ph), 7.93 (2 H, Ph), 8.07 (2 H, Ph). IR (cm^{-1}): 3,298, 1,702, 1,678, 1,649, 1,552. UV, λ_{max}: 340 nm (ε 27,000), 440 nm (ε 880).

*4-[4-(Methyl-palmitoylamino)phenylazo]benzoic acid N-oxysuccinimide ester (**2**)*

To a stirred solution of **1** (0.1 g, 0.20 mmol) and HONSu (0.03 g, 0.30 mmol) in THF (5 mL), cooled in an ice-water bath, DCC (0.07 g, 0.34 mmol) was added and stirring was continued for 4 h at 3°C. The reaction was controlled by TLC on Silufol, solvent system A. The precipitated N,N′-dicyclohexylurea was removed by filtration, and the filtrate was evaporated. The residue was purified on Silicagel L 100/160 column, eluent F to give 0.07 g (58%) of **2**, m.p. 106–107°C, purity established by HPLC 99.5%, R_f(F) 0.66, R_f(D) 0.45. ^{1}H NMR (DMSO-d_6), ppm.: 0.83 (3 H, CH_3), 1.2 (26 H, CH_2), 2.14 (2 H, CH_2CO), 2.93 (4 H, CH_2-Su), 3.24 (3 H, NCH_3), 7.59 (2 H, Ph), 8.01 (2 H, Ph), 8.1 (2 H, Ph), 8.33 (2 H, Ph). IR (cm^{-1}): 1,803, 1,778, 1,760, 1,668. UV, λ_{max}: 344 nm (ε 24,750), 456 nm (ε 860).

*N^3-Boc-N^7-4-|4-(methyl-palmitoylamino)phenylazo |benzoyl-β-homolysine t-butyl ester (**6**)*

Thionyl chloride (0.75 mL, 10.5 mmol) and TEA (1.5 mL, 10.8 mmol) were added to a stirred solution of **1** (0.5 g, 1.01 mmol) in carbon tetrachloride (30 mL). After 60 min. of stirring at room temperature reaction mixture was filtered and the filtrate was evaporated at reduced pressure while keeping the temperature below 36°C. The oily chloride **5** /R_f(A) 0.93/ was dissolved in THF (35 mL) and N^3-Boc-β-homolysine t-butyl ester (0.32 g, 1.01 mmol) was added and then the reaction mixture was adjusted with TEA (about 4 mL) to pH 9–10. After 2 h of stirring at room temperature reaction mixture was filtered and filtrate was evaporated. The residue was diluted with water (100 mL) and adjusted with 1 M HCl to pH 2 then extracted with EtOAc. Extract was washed successively with 10% Na_2CO_3 and water, dried over Na_2SO_4 and evaporated. The residue was purified on Silicagel L 100/160 column with eluent A to give 0.45 g (56%) of **6** as orange oil giving single spot in TLC, R_f(A) 0.37, R_f(G) 0.55. ^{1}H NMR ($CDCl_3$), ppm.: 0.89 (3 H, CH_3), 1.2 (26 H, CH_2), 1.42 (18 H, Bu^t), 2.1 (2 H, CH_2CO), 2.31 (2 H, CH_2COOH), 4.97 (1 H, NHBoc), 6.42 (1 H, NHCO), 7.3–8.0 (8 H, Ph). IR ($CHCl_3$ film, cm^{-1}): 3,335, 1,719, 1,653, 1,542. UV, λ_{max}: 341 nm (ε 23,900), 453 nm (ε 780), $[\alpha]_D^{22} = -7.7$ (THF, c = 1.42).

Compound **9** was prepared from chloride **5** and a solution of N^2-Boc- L-lysine in a mixture of water and THF. The reaction procedure analogous to that for **6** was followed. Yield of **9** 51%.

*N^7-4-|4-(Methyl-palmitoylamino)phenylazo|benzoyl-β-homolysine (**7**)*

Trifluoroacetic acid (0.6 mL) was added to a stirred solution of **6** (0.9 g., 1.14 mmol) in methylene chloride (5 mL). After 24 h at room temperature the solution was evaporated at reduced pressure while keeping the temperature below 22°C. The residue was dissolved in dimethylformamide (5 mL) and N,N-diizopropylethylamine (0.9 mL) was added dropwise. The orange precipitate was filtered, washed with EtOAc to give 0.26 g (36%) of **7**, m.p 219°C, R_f(H) 0.74 (single spot). ^{1}H NMR (DMSO-d_6 + CF_3COOD), ppm.: 0.85 (3 H, CH_3), 1.2 (26 H, CH_2), 2.14 (2 H, CH_2CO), 2.61 (2 H, CH_2COOH), 3.27 (3 H, NCH_3) 7.56–8.1 (8 H, Ph), 8.6 (1 H, NHCO). IR (cm^{-1}): 3,340, 1,638, 1,580, 1,536.

*N^6-4-|4-(Methyl-palmitoylamino)phenylazo|benzoyl-L-lysine (**10**)*

Deprotection procedure of **9** was analogous to that for **6**. Yield of **10** was 72%, m.p. 202–203°C, R_f(H) 0.71 (single spot). ^{1}H NMR (DMSO-d_6 + CF_3COOD), ppm.: 0.85 (3 H, CH_3), 1.18 (26 H, CH_2), 2.16 (2 H, CH_2CO), 3.27 (3 H, CH_3N), 3.91 (1 H, CH), 7.5–8.2 (8 H, Ph), 8.6 (1 H, NHCO). IR (cm^{-1}): 3,310, 1,665, 1,638, 1,586, 1,543.

*N^3-Boc-N^7-4-|4-(Methyl-palmitoylamino) phenylazo|benzoyl-β-homolysine (**8**)*

To a stirred solution of **7** (0.12 g, 0.19 mmol) and 0.5 N NaOH (0.66 mL) in a mixture of i-PrOH (5 mL) and water (2 mL), di-t-butyl dicarbonate (0.08 g, 0.37 mmol) was added. After 24 h of stirring at room temperature the reaction mixture was diluted with water (25 mL), the pH of the solution was adjusted to 5,0 by 5% citric acid (about 3 mL), and extracted with EtOAc. The extract was washed with saturated aqueous NaCl, dried over Na_2SO_4 and evaporated. The residue was purified on Silicagel L 40/100 column, eluent I to give 0.08 g (57%) of **8**, m.p. 134–134.5°C, purity established by HPLC 99.5%, R_f(I) 0.49. ^{1}H NMR ($CDCl_3$), ppm.: 0.88 (3 H, CH_3), 1.22 (26 H, CH_2), 1.41 (9 H, Bu^t), 2.16 (2 H, CH_2CO), 2.58 (2 H, CH_2COOH), 5.13 (1 H, NHBoc), 6.59 (1 H, NHCO), 7.33 (2 H, Ph),

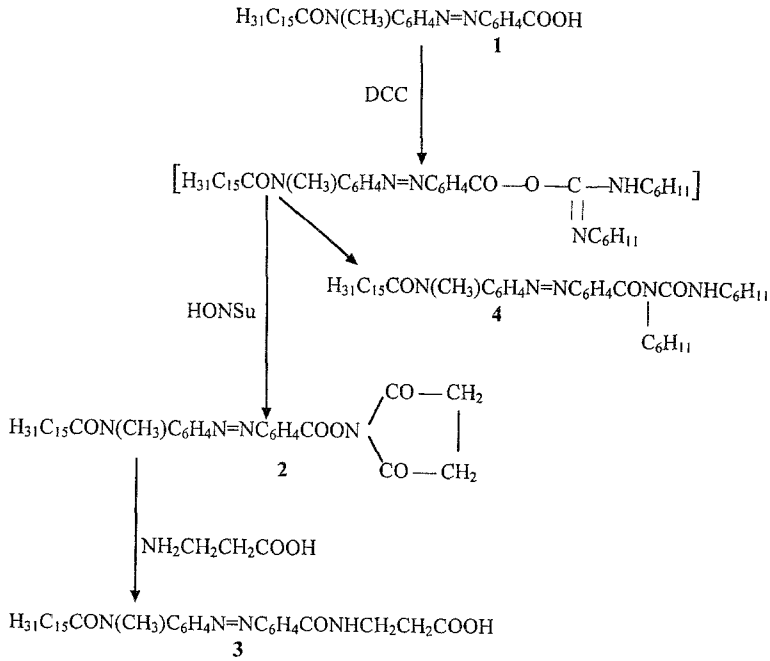
7,84–8.10 (6 H, Ph). IR (cm^{-1}): 3,353, 1,695, 1,638, 1,530. UV, λ_{max}: 342 nm (ε 24,990), 454 nm (ε 840), $[\alpha]_D^{22} = -6$ (THF, c = 1.17).

Results

Starting compound **1** has been synthesized according to procedure by Freimanis (1994). Acylation of β-alanine with azobenzene carboxylic acid chloride **5** afforded the final product **3** with low yields because of the necessity to use water as solvent for β-alanine. Such a reaction medium gives hydrolysis as a side reaction. Synthesis of compound **3** has been achieved by the DCC/HONSu method (Scheme 1). For intermediate compounds **2** and **4**, observed by TLC, independent syntheses have been achieved.

Acylation of β-alanine with 4′-carboxy-4-amino-azobenzene by the DCC/HONSu method has been performed by Denny (1984) and Murphy (1987) with yields from 13% to 37%; side reactions were not investigated. Although the rearrangement of the unstable intermediate of the reaction – O-acylisourea – to N-acylurea is frequently observed, this is the first case when a new surface active azobenzene derivative (**4**) has been synthesized by this reaction.

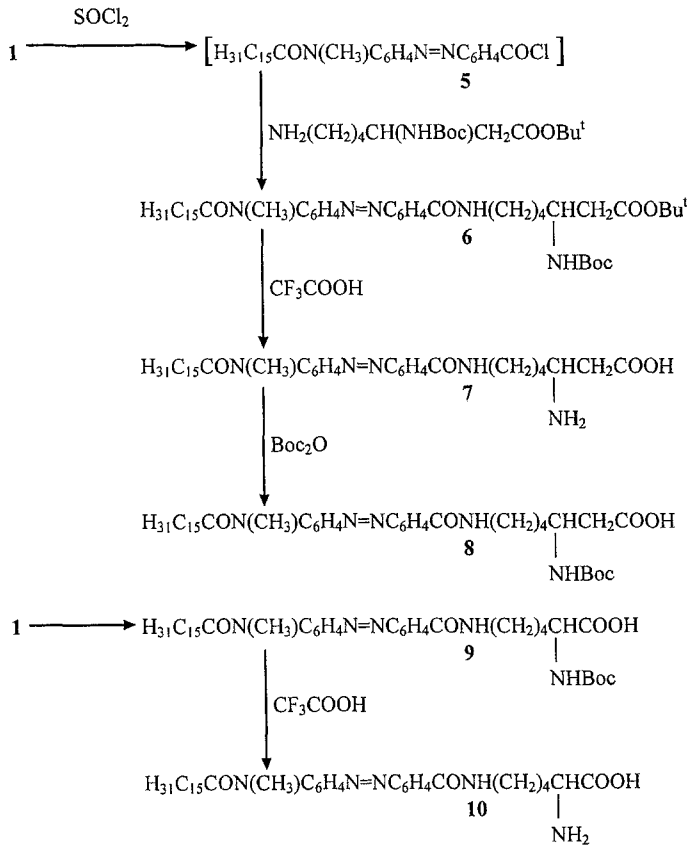
Synthesis of the amphiphilic β-homolysine derivative **7**, containing a azobenzene moiety, has been achieved by acylation of N^3-Boc-β-homolysine t-butyl ester (Markava, 1993) with chloride **5**, and by removing the protective groups from the condensation product **6** (Scheme 2). In order to improve the poor solubility of compound **7** in organic solvents (thus circumventing problems in monolayer technology (Markava, 1993)) the N-protected derivative **8** has been synthesized.



Scheme 1

Lysine derivative **9** has been synthesized by acylation of N^2-Boc lysine by both methods: i.e. DCC/HONSu technology or by using chloride **5**. L-Lysine and β-homolysine derivatives **7** and **10** respectively are insoluble in both water and ordinary organic solvents.

The monolayers spread at the air/water interface have been investigated by means of surface pressure – area per molecule isotherms (see Fig. 1, 2, and



Scheme 2

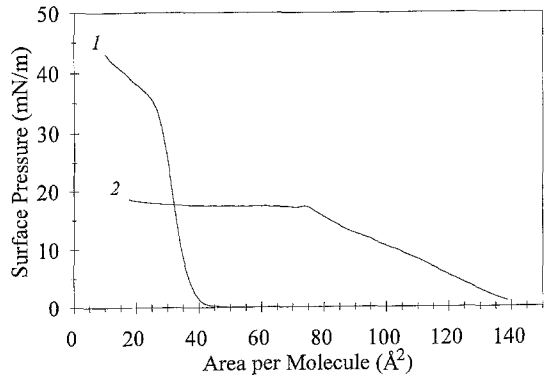


Fig. 1. Surface pressure-area per molecule isotherms of **2** (*1*) and **4** (*2*)

Table 1) and monolayer stability examination (Table 1). In Fig. 1 surface pressure isotherms of intermediate product (**2**) and byproduct (**4**) are plotted.

Monolayers of substance **1** (Freimanis, 1994) have limiting area per molecule 30 Å^2. This value is in good agreement with the smallest molecular cross section of the azobenzene chromophore 25 Å^2 (Xu, 1989). The slightly larger value is a result of $-CH_3$ substitution in the amide group in the "tail". For succinimide surface active derivatives Anzai (1989) has found $A_{\pi\to 0}$ = 30 Å^2. Modelling by molecular mechanics (MM+) has indicated that, in compound **2**, the succinimide and azobenzene ring planes are perpendicular to each other. As one can see from Fig. 2, curve 1, the perpendicular orientation yields value $A_{\pi\to 0}$ = 37 Å^2.

When hydrophobic groups (two cyclohexyl moieties at one end and a palmitoyl group at the opposite end) at both terminals of azo dye are introduced (compound **4**), this increases the probability that the azobenzene rings are oriented with the long axis in the air/water interface plane. This effect is enhanced by hydrophilic groups (carbonyl and amino) in the "bridges" between the hydrophobic and the azo moieties. As one can see from Fig. 1, curve 2, compound **4** forms only an expanded phase with large $A_{\pi\to 0}$ = 144 Å^2. For the formation of the condensed monolayer, with molecular long axes tilt angle close to 0°, it is necessary to immerse the hydrophobic group in water or break

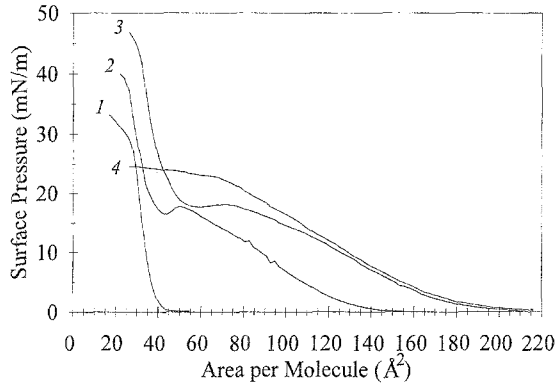


Fig. 2. Surface pressure-area per molecule isotherms of **3** (*1*), **9** (*2*), **8** (*3*), and **6** (*4*)

Table 1. Monolayer data

Compound	Area per molecule Å^2	Collapse pressure mN/m	Monolayer stability (area change) % per h
2	37	31	3.5 (at 20 mN/m)
3	34	27	4.0 (at 20 mN/m)
4	144 (expand.)	16.5	0.0 (at 10 mN/m)
6	175 (expand.)	22	0.0 (at 20 mN/m)
8	175 (expand.)		
	47	44	4.0 (at 30 mN/m)
9	127 (expand.)		
	38	40	15.0 (at 30 mN/m)

the hydrophilic interactions with water. Compression to smaller areas per molecule leads to the monolayer collapse, because both scenarios mentioned above are not energetically favourable.

As seen from Fig. 2 and Table 1 protection of the amino and carboxyl groups with the hydrophobic $C(CH_3)_3$ moiety (**6**, **8**, **9**) yields expanded monolayers with large areas per molecule. Increase of hydrophobicity in the termini of the molecule has the same effect on molecular orientation as in **4** (see above). In the case of **3** (no protection in amino acid residue) a condensed monolayer is formed at the air/water interface (curve 1). In the cases where only the amino group is protected (**8**, **9**) and molecules still have enough hydrophilicity, a phase transition from expanded to condensed monolayer takes place (curves 2, 3). For both **8** and **9** the phase transition pressure is the same – 18 mN/m. Introduction of the second $C(CH_3)_3$ in the polar head of the molecule (**6**) reduces hydrophilicity of the molecule and collapse of the monolayer takes place instead of a phase transition (curve 4).

The limiting area per molecule in the condensed phase depends on the structure of amino acid moiety. Substitution of β-alanine by α-Boc-L-lysine has a weak effect on $A_{\pi\to 0}$ (difference 4 Å^2 per molecule, see Table 1). For comparison: N^6-palmitoyl-L-lysine has a molecular area 27 Å^2 (Landau, 1989). Prolongation of the distance between protected amino- and carboxyl groups yields an increase of $A_{\pi\to 0}$ by 9 Å^2 per molecule. One can notice the same effect in the expanded phase for compounds **8** and **9** (increase of $A_{\pi\to 0}$ by 48 Å^2).

Preliminary experiments on the photoisomerization of solutions of azobenzenes (**2**, **3**, **8**, **9**) in $CHCl_3$, by irradiation with an UV light centered at 360 nm showed that the absorbance at 450 nm increases and that at 340 nm decreases. The photostationary state was reached after time intervals from 30 min to 5 h, depending on the chemical structure of the compound. A similar dependence was observed for *cis*- to *trans*-relaxation of the irradiated samples at room temperature in the dark.

Reversible *trans*/*cis* photoisomerization was observed in the solution as well as in the LB film of **4** (Fig. 3, 4) upon irradiation with UV and visible light.

It is known that the increase of the molecular area along with the decrease of H-aggregation (observed as a shift of the absorption band) enables the photoisomerization of the azobenzene in LB multilayers (Sato, 1994). It seems that this is the case for the LB multilayer from compound **4**. Azobenzene **4** exhibits a molecular area of 144 Å^2 at the surface pressure on the deposition and a slight red shift of the main absorption band at 340 nm going from solution to the LB film (Fig. 3, 4). The absorbance at 345 nm decreases on irradiation with UV light, suggesting *trans*- to *cis*-photoisomerization. In comparison, for compound **3** a molecular area 34 Å^2 was found and a blue shift of the absorption band of about 10 nm was observed, suggesting H-aggregation; the LB multilayer obtained showed no photoisomerization on UV irradiation.

The value of the change in absorbance of **4** multilayer due to photoisomerization was low in comparison with some other azobenzene com-

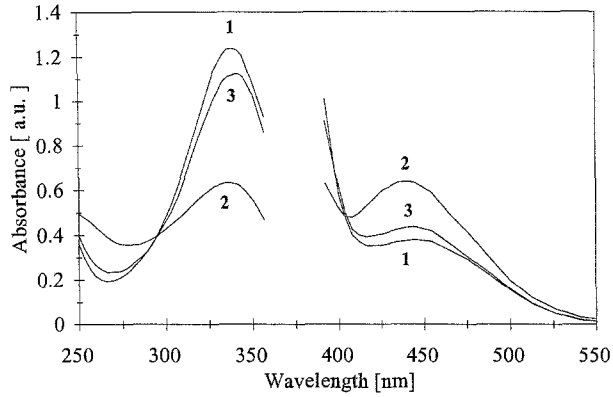


Fig. 3. UV-vis absorption spectra of **4**, solution in $CHCl_3$ 1.92×10^{-4}M, before irradiation (*1*), after 40min of irradiation by UV light (*2*), after 60min. of irradiation by visible light (*3*)

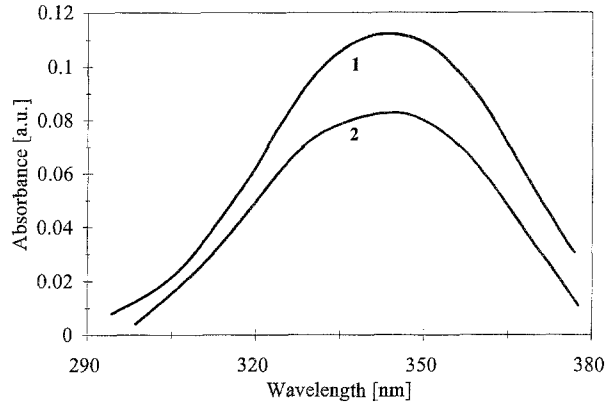


Fig. 4. UV-vis absorption spectra of 16-layered LB film of **4** before irradiation (*1*), after UV irradiation (*2*)

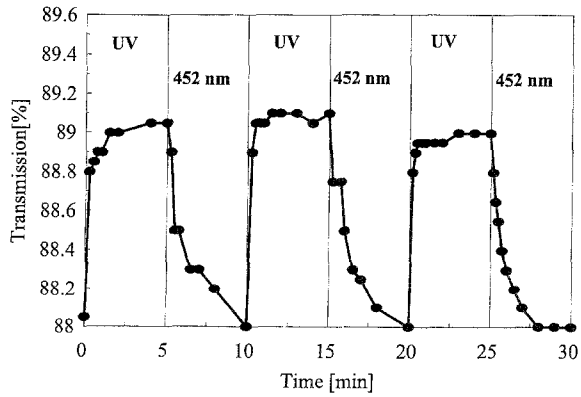


Fig. 5. Reversible cis/trans photoisomerization of 16 – layered LB film of **4**

pounds: 4-octyl-4′-(5-carboxylpentamethyleneoxy)-azobenzene (Liu, 1990), or side chain-type azobenzene polymers (Seki, 1993).

Figure 5 shows the changes in the absorbance at 345 nm on alternate irradiation with UV and visible light. The changes were reversible more than seven times on such irradiation. The absorbance of **4** multilayer with irradiation was saturated in a relatively short time in accord with the results found for the solution of **4** in $CHCl_3$, where the steady-state position was reached after approximately 25 min.

The great difference in the rates of trans/cis photoisomerization, limiting area per molecule on the air/water interface, character of π-A isotherms, collapse pressure and stability of monomolecular layers, depending on the chemical structure of the compound, gives a chance for variation of the properties of the materials for photoresponsive mono- and multilayers.

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