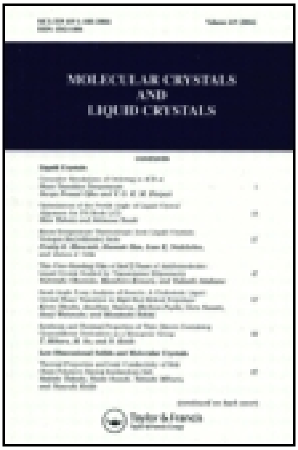

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Photochromism of Some Azobenzene Derivatives in Thin Films as a Function of the Chemical Properties of the Molecule

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Photochromism of Some Azobenzene Derivatives in Thin Films as a Function of the Chemical Properties of the Molecule

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The effect of the modification of the structure of azobenzene molecule by introduction a variety of functional groups on the photoisomerization in Langmuir-Blodgett and vacuum evaporated films has been investigated. The switching effect of the absorption, the surface potential and the electrical properties in thin layers of compounds has been discussed. A novel approach to the design of azobenzene amphiphiles, such as introduction of large bulky substituents in the molecule providing for a free volume necessary for the trans-to-cis photoisomerization, gave a number of valuable photochromic materials for investigation of reversible optically induced switching processes.

Keywords: azobenzene derivatives; Langmuir-Blodget films; vacuum evaporated films; optically induced switching; absorption; surface potential

1. INTRODUCTION

Azobenzene derivatives are typical materials displaying reversible photoisomerization and are of great potential for application in Langmuir-Blodgett (LB) films as materials for optical switching systems[1,2]. The azobenzene unit undergoes trans-to-cis isomerization by irradiation with UV light centered at wavelength of main absorption maximum of molecule (~360nm). The reverse process is observed by irradiation with visible light centered at wavelength corresponding

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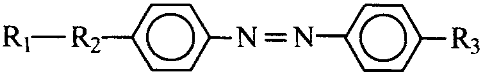
* Corresponding author

to absorption maximum at 450nm. Photoisomerization of azobenzenes in solid phase is frequently studied in polymeric materials[3], because in LB films of monomeric compounds a large dynamic motion, required during the trans-to-cis isomerization, is significantly retarded due to the close packing of molecules in layers and H-aggregation of chromophores[4]. There are only a few known examples of reversible photochromic behavior of some azobenzene derivatives "pre-treated' with UV irradiation[5], or in mixed monolayers of amphiphilic azobenzene derivative and spacer molecule[6].

Recently we have proposed a novel approach to the design of azobenzene amphiphiles, such as introduction of large, bulky functional groups in the molecule providing for a free volume necessary for the trans-to-cis photoisomerization, since the cross-sectional area of the cis isomer is larger than that of the trans isomer.

2. OBJECTS

In order to investigate the relationship between the optically induced switching processes and the molecular alignment, systematic modification of molecule was made while maintaining the same azobenzene unit:



SCHEME 1

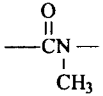
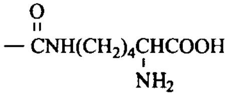
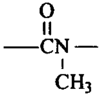
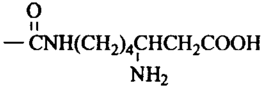
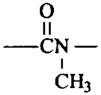
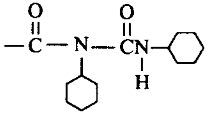
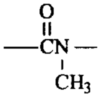
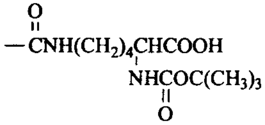
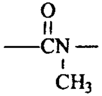
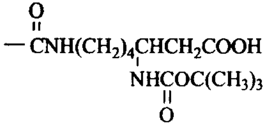
We have started with amphiphilic (methylacylamino)azobenzene derivative **1**, containing in the molecule a tertiary amide group along with the carboxylic moiety[7]. In this group three derivatives with different length of alkyl chain were synthesized (see compounds **1a, 1b** and **1c** Table I).

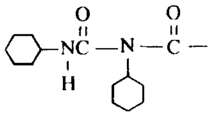
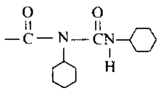
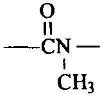
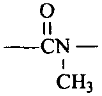
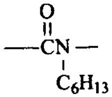
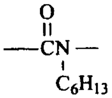
Another group of azobenzene derivative **2** containing the secondary amide linkage -NHCO- was synthesized (see compounds **2a, 2b** Table I)[8].

Compounds **1** and **2** were used for both as a model compounds for the investigation of the dependence of the photosensitivity of LB multilayers on the chemical structure of azobenzene derivatives and as raw material for the preparation of a number of azobenzenes modified by the introduction of α- and β-amino acid moieties (compounds **3, 4** and **5**)[9] or N,N'-dicyclohexylurea fragment (compound **6**)[9]. Azobenzenes **4** and **5** are insoluble in common organic solvents, used in monolayer technology. In order to improve the poor solubility of these compounds, their N-t-butyloxy carbonyl derivatives **7** and **8** correspondingly have been synthesized.

TABLE I Sample code, molecular structure, properties of Langmuir monolayer and LB film of the synthesized azobenzene amphiphiles

	R₁	*R₂*	*R₃*	π_{col} *(mN/m)*	*Area/mol* ($\AA^2$) ($A_{\pi\to 0}$)	$\pi_{deposit}$ *(mN/m)*	λ_{sol} *(nm) (CHCL₃)*	λ_{LB} *(nm)*	*Isomer. in. the LB film*
1a	$H_{23}C_{11}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{\mid}}{N}-$	$-COOH$	27	30	21	340	----	----
1b	$H_{31}C_{15}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{\mid}}{N}-$	$-COOH$	35	30 – 33	21	340	330	No
1c	$H_{35}C_{17}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{\mid}}{N}-$	$-COOH$	42	30 – 33	21	340	333	No
2a	$H_{23}C_{11}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle H}{\mid}}{N}-$	$-COOH$	45	See text	----	371[a]	----	Yes
2b	$H_{31}C_{15}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle H}{\mid}}{N}-$	$-COOH$	40	See text	25	371[a]	325[a]	No
3	$H_{31}C_{15}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{\mid}}{N}-$	$-\overset{\overset{\displaystyle O}{\|}}{C}NH(CH_2)_2COOH$	27	34	25	341	~ 320	No

	R_1	R_2	R_3	π_{col} (mN/m)	*Area/mol* $(\AA^2)$ $(A_{\pi\to 0})$	$\pi_{deposit}$ (mN/m)	λ_{sol} *(nm)* $(CHCL_3)$	λ_{LB} *(nm)*	*Isomer. in. the LB film*
4	$H_{31}C_{15}-$	 $-\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{\mid}}{N}-$	 $-\overset{\overset{O}{\|}}{C}NH(CH_2)_4\underset{\underset{NH_2}{\mid}}{C}HCOOH$	Not soluble in solvents used for LB technology					
5	$H_{31}C_{15}-$	 $-\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{\mid}}{N}-$	 $-\overset{\overset{O}{\|}}{C}NH(CH_2)_4\underset{\underset{NH_2}{\mid}}{C}HCH_2COOH$	Not soluble in solvents used for LB technology					
6	$H_{31}C_{15}-$	 $-\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{\mid}}{N}-$		16.5	144	14	339	345	Yes
7	$H_{31}C_{15}-$	 $-\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{\mid}}{N}-$	 $-\overset{\overset{O}{\|}}{C}NH(CH_2)_4\underset{\underset{NH\underset{\underset{O}{\|}}{C}OC(CH_3)_3}{\mid}}{C}HCOOH$	40 $(\sim 15)^b$	38 $(\sim 127)^b$	Mono-layer is not stable	341		----
8	$H_{31}C_{15}-$	 $-\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{\mid}}{N}-$	 $-\overset{\overset{O}{\|}}{C}NH(CH_2)_4\underset{\underset{NH\underset{\underset{O}{\|}}{C}OC(CH_3)_3}{\mid}}{C}HCH_2COOH$	44 $(\sim 16)^b$	47 $(\sim 175)^b$	----	342	----	----

	R₁	*R₂*	*R₃*	π_{col} *(mN/m)*	*Area/mol* (Å^2) ($A_{\pi\to 0}$)	$\pi_{deposit}$ *(mN/m)*	λ_{sol} *(nm)* *(CHCL₃)*	λ_{LB} *(nm)*	*Isomer. in. the LB film*
9				45	90	21	336	345 320^c	Yes
10a	$H_{31}C_{15}-$	 $-\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{\vert}{N}}-$	$-SO_2NH_2$	37	35	---	341	----	----
10b	$H_{31}C_{15}-$	 $-\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{\vert}{N}}-$	$-SO_2NH(CH_2)_2COOH$	43	30	36	341	316	Yes
11a	$H_{31}C_{15}-$	 $-\overset{O}{\overset{\|}{C}}\underset{C_6H_{13}}{\underset{\vert}{N}}-$	$-SO_2NH_2$	27 (~10)^b	90 (~118)^b	16	336	349	Yes
11b	$H_{31}C_{15}-$	 $-\overset{O}{\overset{\|}{C}}\underset{C_6H_{13}}{\underset{\vert}{N}}-$	$-SO_2NH(CH_2)_2COOH$	45 (~15)^b	77 (~118)^b	22	342	347	Yes

a. solution in DMF;
b. phase transition pressure and expanded phase limiting area;
c. VE film

4,4′-Azobenzene dicarboxylic acid di(N,N′-dicyclohexylurea) **9** has been synthesized in order to verify the proposition about cyclic hydrophobic groups, instead of linear alkyl chains (compound 6), being favorable for loose packing of azobenzene moieties in LB mono- and multilayers, which improve their photosensibility[10].

Another line of our investigations has been directed on compounds **10** and **11** bearing an electron acceptor (SO_2) and electron donor (N-alkylamino) groups at the opposite ends of the azobenzene moiety[11,12,13]. Molecules **10** and **11** are characteristic with higher permanent dipole moment in comparison with other azobenzene derivatives studied in this work.

3. LB MULTILAYERS

The multilayers of azobenzene derivatives were prepared by Langmuir-Blodgett (LB) technique[9]. The π-A isotherms were obtained in a computer controlled Langmuir through by the "step-by-step" method. The concentration of the spreading solutions in $CHCl_3$ was in range $1x10^{-3}$-$3x10^{-4}$M. Double distilled water (pH 5.8) was used as subphase. The typical isotherms of some compounds are shown in Figure 1.

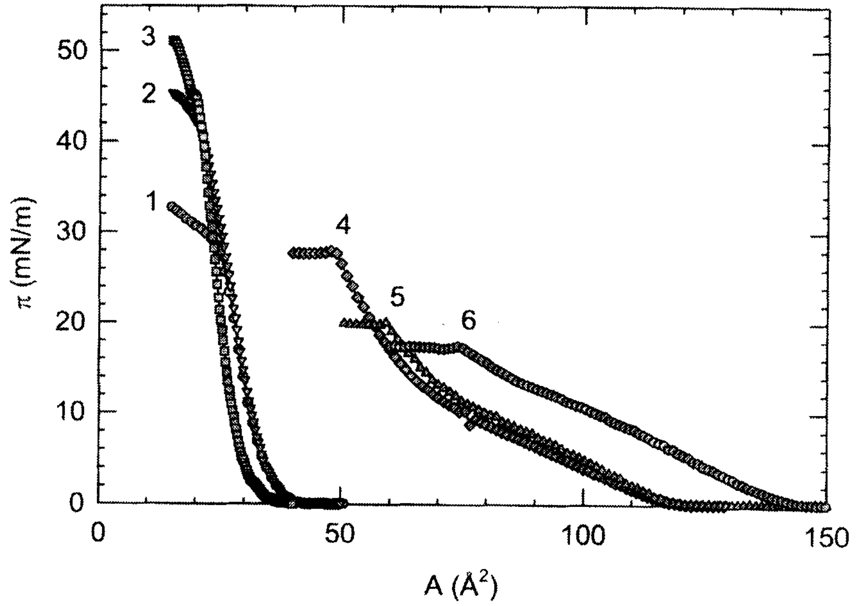


FIGURE 1 Surface pressure/area per molecule isotherms of compounds **3**(1), **10a** (2), **10b** (3), **11b** (4), **11a** (5) and **6** (6)

In the case of compound **2a** the poly(diallyldimethylammonium chloride) (PDMDAAC) polymer with $CdCl_2$ was used as subphase. It is known that the use of water subphase containing water soluble polycation (for example PDMDAAC) makes the fabrication of LB films from amphiphilic anionic azobenzenes possible. The LB multilayers were deposited onto hydrophilic or hydrophobic quartz, sapphire, glass, and ITO glass substrates. For electrical measurements the LB multilayers were deposited on coplanar sandwich-type cells with Au, Cr, ITO or SnO_2 electrodes. The deposition procedure is described in References[7,8,14,15,16]. The type of deposition was determined by observing the decrease in surface area during transfer of the monolayer to a solid substrate. The values of limiting area per molecule $A_{\pi\rightarrow 0}$ obtained from π-A isotherms (π-A) are shown in Table I.

Structural studies of monolayers of molecules **1b, 1c** carried out by Atom Force Microscopy (AFM) showed non-uniform domain-type covering of glass substrate. However, the high ordered array of **1b** molecules of hexagonal packed structures was observed in domains. The area per molecule measured directly from the AFM images is $A=23\pm2Å^2$ [14]. It was found that there is a linear correlation between limiting area per molecule $A_{\pi\rightarrow 0}$ and cis/trans isomers ratio in spreading solutions. The limiting area per molecule estimated from π-A isotherms is $25\pm5Å^2$ for the trans isomer and $60\pm5Å^2$ for the cis isomer[7]. These values correspond to nearly vertical orientation of azobenzene moiety in trans isomer molecules in monolayers and almost horizontal in cis isomer.

The main absorption maximum of the azobenzene chromophore is the π-π^* transition at spectral region 336–370nm for which the transition dipole is directed along the long axis of the azobenzene moiety. Another absorption maximum due to n-π^* transition is present in the visible spectral region at 450nm. **1b** and **1c** exhibit a slight blue shift (about 10nm) of the main absorption band at 340nm in going from $CHCl_3$ solution to the LB film [8,16] (see Table I), In the case of compound **2b** the blue shift in going from DMF solution to LB film is considerable and yields about 45nm. The molecular area was not determined from π-A isotherms because DMF used as a volatile solvent is miscible with water and promote an unknown amount of the amphiphiles to be dissolved in the subphase. The another possibility to deposit compound **2a** onto Si wafer was using subphase with $CdCl_2$ and PDMDAAC polymer[17]. In this case the value of the limiting area per molecule $23Å^2$, obtained by AFM, showed close packing of molecules in monolayer. For compound **3** a value of limiting area per molecule of $34Å^2$ was found (see Figure 1, curve 1) and a blue shift of the main absorption band of about 20nm was observed in going from $CHCl_3$ solution to LB film. The blue shift of the main maximum in the UV spectral region of the LB film in comparison with the spectrum of the solution is an indication of the

H-aggregation of the azobenzene chromophores, where the chromophores are oriented parallel mutually[4,18]. In the case of LB films it is not possible to distinguish between shift due to change in the distance of the chromophores and a change of orientational distribution of the transition dipole moments, because in the contrast to the situation in a crystalline sample in the LB film, there is the superposition of several structures with a distribution in the distance and the orientation of the chromophores. In order to attribute the shift of the maximum in the UV spectral region to molecular packing in LB layer the additional information of the structure of molecules is necessary.

Azobenzene **6** exhibits limiting molecular area of 144Å^2 (see Figure 1, curve 6) and, contrary to previous cases, a slight red shift of the main absorption band at 345nm in going from solution to the LB film. Azobenzene **9**, in comparison with the compound **6** form more stable monolayer and exhibit the value of limiting area per molecule of 90Å^2. LB multilayer of azobenzene **9** on hydrophilic quartz substrate exhibit a negligible red shift of the main absorption band going from solution in $CHCl_3$ to LB film.

For LB multilayers of compounds **10a** and **10b** with the smallest values limiting area per molecule (see Figure 1, curves 2 and 3), a blue shift (up to 25nm) of the main absorption band was observed on going from solution to LB film. In the LB films of compounds **11a** and **11b**, a negligible red shift of the main absorption band (by about 5nm) was observed. When a hexyl group is introduced, resulting in a double chain chemical structure of the molecules **11a** and **11b**, a phase transition from expanded to a condensed monolayer takes place (see Figure 1, curves 4 and 5). The value of limiting area per molecule in the condensed phase undergoes a dramatic increase from compounds **10a** and **10b** ($A_{\pi\rightarrow 0}$=30–34Å^2) to the double chain derivatives **11a** and **11b** ($A_{\pi\rightarrow 0}$=77–90Å^2). It seems that increased steric interaction in the N-alkyl-N-acyl fragment, resulting from the more bulky hexyl group compared with the methyl group, causes the structural differences that give rise to the increase in the limiting molecular area of compounds **11a** and **11b**. The larger limiting areas of compounds **11a** and **11b** result in larger distances between azo chromophores and weaker intermolecular interactions and, contrary to **10a** and **10b**, a red shift of main maximum was observed (see Table I).

4. VACUUM EVAPORATED FILMS

The thin films of compound **9** were prepared by vacuum evaporation (VE) at temperature 270°C in vacuum 10^{-6}mmHg. The films with thickness of 0.3μm were deposited on glass or quartz substrates. For investigation of electrical properties vacuum evaporated Au was used as electrode in coplanar cells. The AFM images show polycrystalline structure of the film with value of average roughness RMS=270Å [10]. Contrary to LB films of compound **9**, the blue shift of 16nm of the main maximum in going from solution to film was observed. This may be interpreted as aggregation in the form of H-aggregates.

5. PHOTOISOMERIZATION IN LB MULTILAYERS

5.1 Optically induced changes of absorption spectra

It is known that azobenzene chromophore exhibit trans-cis isomerization process, when irradiation with UV light at the main absorption maximum is employed. Reverse cis-trans isomerization takes place by thermal treatment or irradiation with visible (around 450nm) light. UV light induced formation of the cis isomers is the fact supported by the decrease of the absorbance in the main absorption maximum. Therefore reversible trans-cis isomerization reaction in solutions, LB films as well as vacuum evaporated films can be readily proved by optical absorbance spectroscopy.

Experiments on the photoisomerization of solutions of azobenzenes **3, 6, 7** and **8** in $CHCl_3$ by irradiation with an UV light centered at 360nm show, that the absorption at 450nm increases and at 340nm decreases. Samples with the concentration of the order of 10^{-4}M were irradiated with the non-polarized light by Xenon lamp DKS-L-250i using filter centered at λ=360 nm for UV light and interference filter at λ=452 nm for VIS light[9]. Typical absorption spectra in dependence on irradiation with UV and visible light are shown in Figure 2.

Absorption spectroscopy was employed to investigate the photoisomerization kinetics. The absorption spectra were recorded over different time intervals of the irradiation with UV or visible light until a photostationary state was reached. The dependence of the value of absorbance at maximum in visible spectral region on irradiation time was obtained. The best fit of the experimental points was obtained by simulating with an exponential function:

$$\frac{D_0 - D}{D_0} = A\exp(-t/\tau), \tag{1}$$

where D_0 is optical density before irradiation, D is optical density during irradiation, A is the pre-exponential factor and τ is the time constant, which characterizes the response of the process to irradiation.

The photostationary state of absorbance was reached after time intervals from 3min to 5hours, depending on the chemical structure of the compound. The time

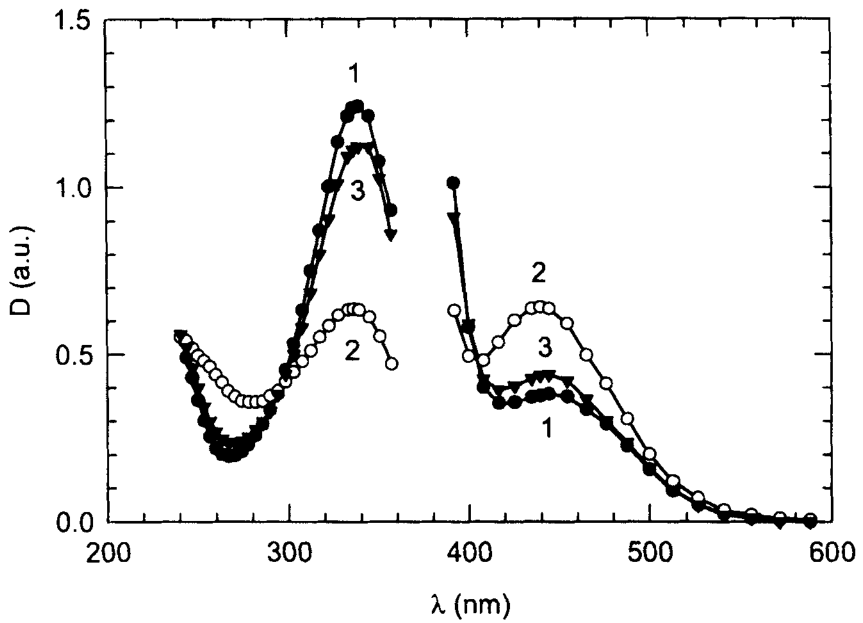


FIGURE 2 UV-visible absorption spectra D(λ) of compound **6** 1.92x10^{-4}M solution in $CHCl_3$ before irradiation (1), after 40min of irradiation by UV light (2) and after 60min of irradiation by visible light (3)

constant for more compounds was in the range from 3 to 10 min. In the case of amphiphilic β-alanine derivative (**3**) and β-homolysine derivative (**8**) the response to irradiation was very slow and the time constant reached value τ=5hours. Consequently, these derivatives were not interesting for further investigations.

Reverse process was slower when compared to those of the trans-to-cis isomerization. The exponential-type time dependence was observed for cis-to-trans relaxation of irradiated samples at room temperature and the value of the time constant was about 2 times larger. We made some attempts at photoisomerization of azobenzene **1a** in a monolayer at water/air interface. However on irradiation with UV light at constant pressure of 10 mN/m no changes of the monolayer covered area has been observed. Close packing of azobenzene groups probably blocks the trans-to-cis photoisomerization.

In experiments with LB layers, the samples were irradiated with light propagating normal to the sample surface. **1b**, **1c** and **2a**, **2b** LB films showed no changes of absorbance on UV irradiation[8]. As follows from AFM method, the irradiation with an UV light centered at 365nm destroys alignment as well as the long range ordering of molecules[14]. A partial long range ordering is recovered back in three hours after removing UV light. Since the molecules are very closely packed in the monolayer formation, the distance between molecules is too small to provide enough space for the full isomerization from trans to cis of all the molecules in the monolayer. Consequently the changes of the absorbance by irradiation might be less than experimental resolution of spectrometer. The significant modifications are observed in frontier regions between two crystalline domains of different orientation and in the edges of the slabs, places where the free volume available for molecular arrangement is likely to be larger[14]. Our observations provide experimental support to the suggestion put forward by Liu and collaborators[5] that a pretreatment of an LB film with UV light can induce a rearrangement of the molecules in the hole and defect regions, resulting in reversible photoisomerization of material. The LB multilayers obtained from compound **3** exhibiting molecular area of 34Å show no changes of the value of the absorbance in main maximum on UV irradiation.

One of the most promising azobenzene derivatives for trans-cis photoisomerization was compound **6**. The changes in the absorbance at 345nm on alternate irradiation with UV and visible light are shown in Figure 3a.

The changes were reversible for more than seven times on such irradiation. It has been well established[19,20] that the kinetics of processes occurring in condensed matter should be described as first-order processes according to the equation (1) (see Figure 3b). The absorbance of **6** multilayer with UV irradiation was saturated in a relatively short time (τ=9s) in comparison with the solution of compound **6** in $CHCl_3$ where the value of time constant was approximately 7min. It is known that the increase of the molecular area along with the decrease of H-aggregation (observed as a shift of the absorption maximum) enables the photoisomerization of the azobenzene in LB multilayers[4,18]. It seems that is the case for the LB multilayer of compound **6**. The bulky N,N'-dicyclohexyl urea moiety might cause looser packing of azo units in the monolayers and, consequently, the molecular reorganization by photoisomerization might proceed readily. The back isomerization by irradiation with visible light was slower and reached value τ=90s (see Table II).

Azobenzene **9**, containing two cyclic hydrophobic groups, undergo reversible trans/cis photoisomerization on alternate irradiation with UV and visible light. The cycles could be repeated several times. The molecules seems to be more tightly packed in the LB films of compound **9**, resulting in much larger value of response time (τ=3min) to UV irradiation and in value of optical density in the main absorption band two times of magnitude less in comparison with these for azobenzene **6**.

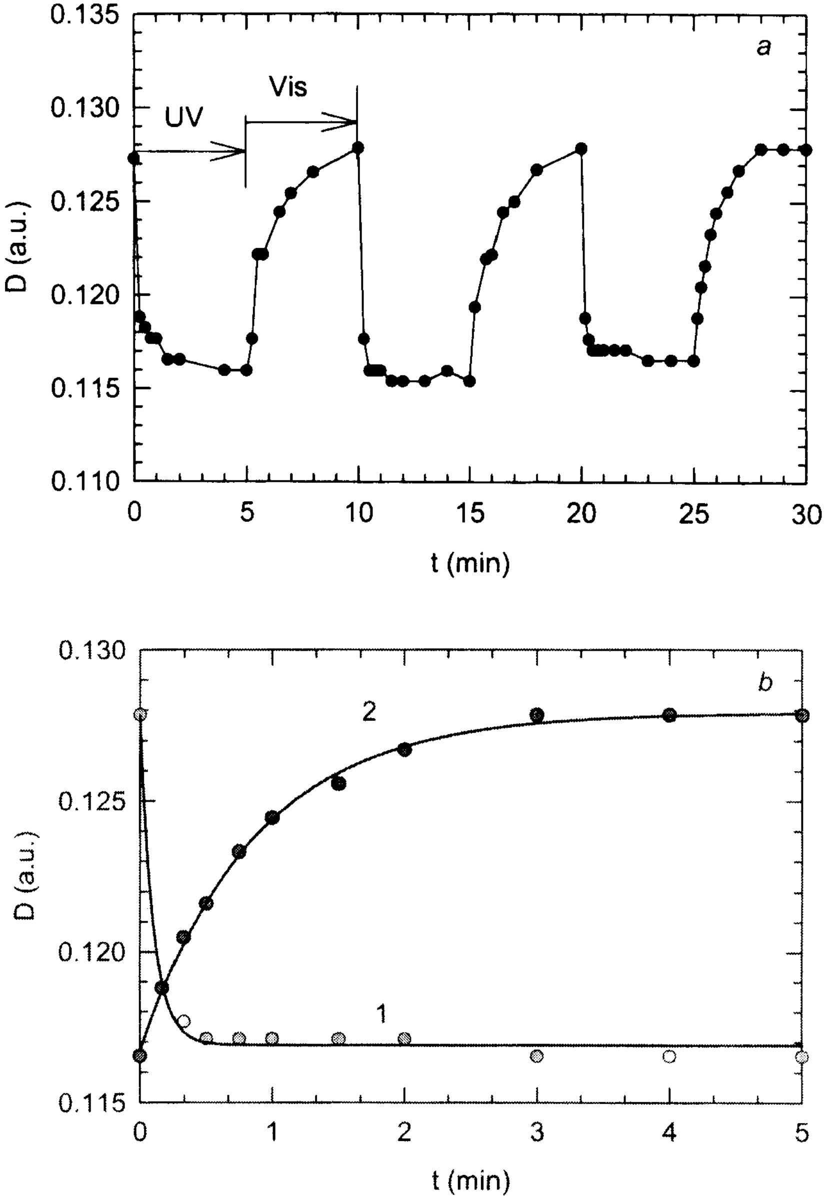


FIGURE 3 (a) Reversible trans-cis isomerization of 16 layered LB film of compound **6** with light centered at 360nm (UV) and with light centered at 452nm (VIS). (b) Photoisomerization kinetics of the changes of the absorbance D(t) on irradiation with UV light (1) and VIS light (2). The curve fits by exponential function are shown as solid lines

The multilayer assembly of compound **10b** shows no photoisomerization on UV irradiation because of close packing of molecules in monolayer. In contrast the LB multilayers from **11a** and **11b** exhibit reversible trans/cis photoisomerization on alternate UV and visible light irradiation, confirming the proposition that the increase in molecular area along with the decrease or absence of H-aggregation in the multilayers enables its photoisomerization[4,18] In LB films of investigated azobenzene derivatives, when aggregation of chromophores takes place, the trans isomers transformation to cis isomers is restricted and consequently the observed value of the changes of absorbance on irradiation are small or not at all. The double-chain structure in the N-alkyl-N-acyl fragment (**11a, 11b**) or the bulky N.N′-dicyclohexyl urea moiety (**6, 9**) might cause looser packing of azobenzene units in the monolayers and, consequently, the molecular reorganization by photoisomerization might proceed more readily.

TABLE II The value of the change of the value of optical density $\frac{D_0 - D}{D_0}$ in the main absorption band of LB film and the change of the surface potential ΔU_S of LB monolayer of compounds **6, 9, 10b, 11a** and **11b**and VE film of compound **9** on irradiation with UV (trans-cis) and visible light (cis-trans)

Film		*Absorption of thin film*				*Surface potential of thin film*			
		Trans-cis		*Cis-trans*		*Trans-cis*		*Cis-trans*	
		$\frac{D_0 - D}{D_0}$	τ *(min)*	$\frac{D_0 - D}{D_0}$	τ *(min)*	ΔU_S *(mV)*	τ *(min)*	ΔU_S *(mV)*	τ *(min)*
2a		---				5	7	5	7
6	LB	0.09	0.14	0.09	1.5	17	6.2		
9	LB	0.04; 0.01	0.17; 2.8	0.04	2.40	40	3.7	26	5.0
	VE	no observed				8	8.0	1; 8	0.8; 2.3
10b	LB	No observed				2			
11a	LB	0.10	0.74	0.07	2.68	17	2.1	37	4.1
11b	LB	0.10	0.16	0.10	1.03	15–6	4.6–6.7	13–9	2.5–2.9

5.2 Switching effect of the surface potential

The surface potential U_S of the thin film depends on both – the packing density and the orientation of molecules. The monolayer is treated usually as a uniform assembly of molecular dipoles, which give rise to a polarization within the layer. The direction of polarisation inferred from positive sign of the change in the surface potential with respect to the clean gold electrode. It is shown that the surface potential can be related to dipole moment normal to the plane of the monolayer of molecules $\mu_p = \varepsilon\varepsilon_0 A U_s$, where A is the average area occupied by the molecule[21]. It is shown that for trans isomer of azobenzene moiety the value of molecular dipole moment is zero, but for cis isomer the value of dipole moment is of μ=3D[22]. Azobenzene derivatives containing polar sulfonyl group posses high value of molecular dipole moment also in trans configuration. The value of the dipole moment of alkyl chain is low of the order of 0.4D[23]. The value of molecular dipole moment of monolayer can be considered as sum of dipole moment of the head group with azobenzene moiety and hydrocarbon tail. The photoisomerisation process causes the changes of the value of the molecular dipole moment in the head group of azobenzene derivatives. Consequently, the changes of molecular dipole moment normal to the surface of the film emerge and the changes of the surface potential ΔU_S might be observed. The investigation of the changes of the surface potential on irradiation with alternate visible light and ultraviolet light characterises the photoisomerisation process in monolayer. The measurements of the surface potential were done by Besocke Delta PHI GmbH/ Kelvin control equipment using Kelvin Probe technique[24] with the resolution of measuring values was less than 1mV. The samples were irradiated by Xenon lamp using filters centered at 360nm with light intensity about 1.5mW/cm^2 and 450nm with light intensity about 2mW/cm^2.

For the most perspective compounds (**6, 9, 11a, 11b**), following from photoinduced changes of the absorbance of the main absorption maximum, the changes of the value of surface potential ΔU_S on altering irradiation of LB mono- and multilayers on polycrystalline Au layer were investigated (see Table II). The value of changes of ΔU_S was in the range from 8mV (compound **11b**) till 40mV (compounds **9** and **11a**). In all cases the reversible process was observed (see Figure 4a). These values of ΔU_S were small in comparison with monolayer of a mixture of amphiphilic azobenzene pyridinium derivative and dimiristoylphosphatidic acid on air-water interface, where the changes of the surface potential of the order of 100mV were observed[11].

The kinetics of the changes of the surface potentials of LB multilayers of azobenzene compound **11b** on sputtered Au thin film is shown in Figure 4b. The best fit of the experimental points was obtained by simulating the potential data with a simple exponential decay or rise in dependence on irradiation with UV or visible light. The approximation of the kinetic of the value of ΔU_s gave the value of time constant in the range from 2 to 7min in dependence on compound and structure of Au film as well (see Table II).

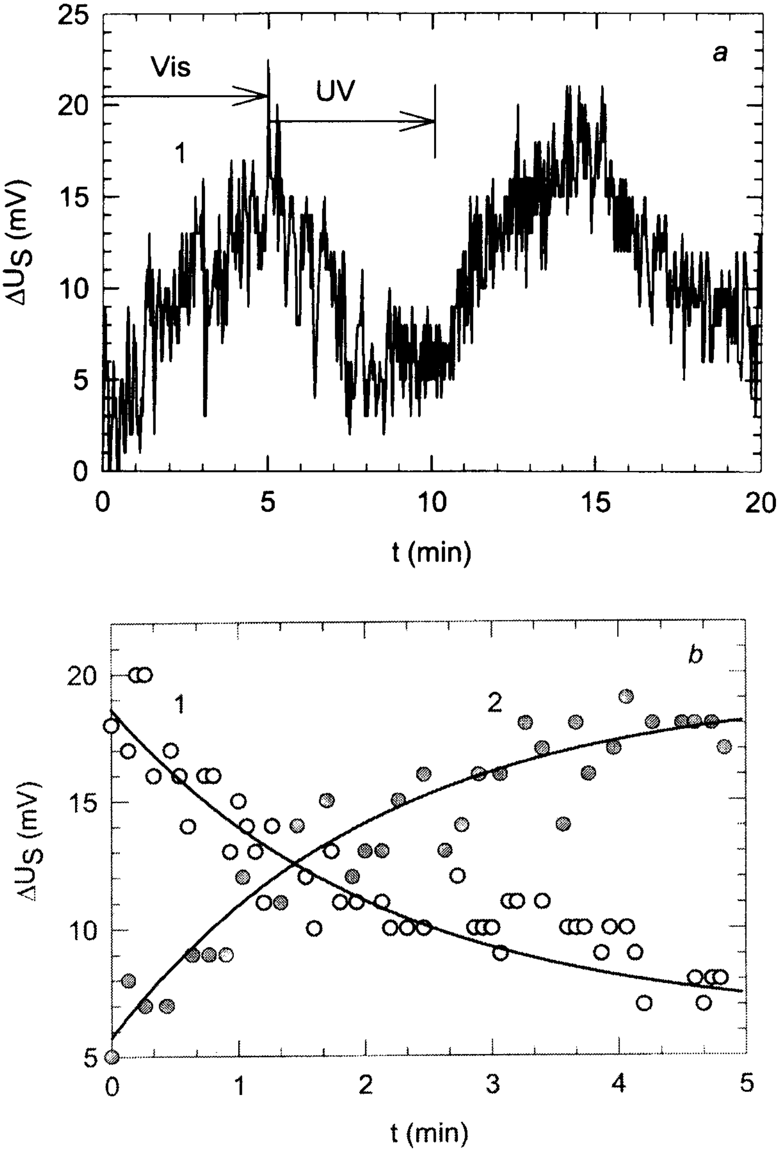


FIGURE 4 (a) Photoisomerization kinetics of the changes of the surface potential on irradiation $\Delta U_S(t)$ with light centered at 360nm (UV) and with light centered at 452nm (VIS) of LB monolayer of compound **11b** on sputtered Au surface. (b) Photoisomerization kinetics of the changes of the surface potential $\Delta U_S(t)$ on irradiation with UV light (1) and VIS light (2). The curve fits by exponential function are shown as solid lines

It is shown that the process of trans-to-cis isomerisation of the azobenzene derivatives in LB film takes place in 200μs both for low molecular weight and polymeric liquid crystals[2]. Structural investigations of LB layers showed close packing of molecules in domains[13,14] that prevent azobenzene moiety to twist going from trans to cis configuration. The last reason possibly might explain the fact that the kinetic of decrease or increase of the value ΔU_S is slow in comparison with the value published in Reference[2].

In order to investigate the influence of the structure of Au films on the optically induced switching of the values of ΔU_S and τ, the studied azobenzene derivatives were deposited on Au thin films prepared by sputtering in Ar atmosphere and by vacuum evaporation on glass substrate. The average roughness (RMS) of both types of Au thin films was obtained by AFM measurements. The value of RMS of vacuum evaporated Au thin film on glass was of the order of 70Å and for sputtered Au – RMS=50Å [25]. In was shown for all studied derivatives, that in the case of LB layer deposited on sputtered Au thin film the value of ΔU_S was larger and the photoisomerization process was faster in comparison with one deposited on the vacuum evaporated Au film. For example in case of compound **11b**, the value of ΔU_S decreased from ΔU_S=15mV to ΔU_S=6mV, but the value of the time constant τ of the trans-to-cis isomerization process increased from τ=4.5min to τ=7min. As follows from experimental results there are not direct relationship between the roughness of the Au film and the values of ΔU_S and τ. In the case of vacuum evaporated Au film on glass substrate the value of RMS is highest, but the value of the changes of surface potential is very small and response time to irradiation is slow. Investigations of Au evaporated thin films by X-ray diffraction spectra have shown highly ordered structure of Au atoms in crystallites, which may causes closed packed structure of azobenzene molecules.

6. PHOTOISOMERIZATION IN VACUUM EVAPORATED FILM

Structural studies of VE thin films of compound **9** carried out by AFM showed polycrystalline structure with size of crystallites of the order of 500Å. Our attempts to observe changes of the absorbance were unsuccessful irradiating by UV and visible light half an hour and after applying of several cycles of alternate irradiation as well. The photoisomerization of azobenzene chromophore in VE film appears to be hindered by the more dense packing of molecules in crystallites in comparison with that for related LB films.

The random orientation of the molecules in VE film causes total value of the dipole moment of the film may be close zero. When sample was irradiated firstly with UV and visible light no change of the value of the surface potential was observed. After several repeating cycles of irradiation the optically induced switching of the value of ΔU_s of 8mV appeared. During UV and visible irradiation, where trans-cis isomerization took place, the rearrangement of molecules on the surface of the film emerged. Such optically "pretreated" molecules on the surface formed stable ordered layer, which provide a favorable environment for the reversible photoisomerization. The value of the surface potential is determined by the orientation of the molecules on the surface of the film and, consequently, the changes of the value of the surface potential due to photoisomerization is observed. This assumption probably explains fact that we do not observe switching effect of absorbance. The changes of the absorbance, which is caused by isomerization of the molecules on the surface of the film, might be miserable in comparison with the value of total absorbance of the film and less than experimental resolution of spectrometer. The switching process of the surface potential was stable and reversible. The value of ΔU_S was several times less and the trans-to-cis isomerization process, described by first order kinetic, was slower with time constant of 8min in comparison with LB monolayer (see Table II). The back isomerization was fitted by double exponential function and might be involve at least two mechanisms characterized by different time constants.

7. ELECTRICAL PROPERTIES

It is shown that in LB films of azobenzene derivatives the reversible changes of electrical conductivity on alternating irradiation take place[26]. The azobenzene derivative containing azobenzene and unit, which consist of pyridinium acceptor and TCNQ donor, shows reversible changes in conductivity of 30%. In this case the isomerization of azobenzene unit controls the conductivity associated with the conductive unit.

In order to investigate electronic properties of our azobenzene derivatives, electrical properties were studied in the regime of space charge limited currents (SCLC). In order to obtain energy structure of local trapping states (energy depth in energy gap E_t and total density of given set of traps N_t), the dependence of activation energy of electrical conductivity E_a on applied voltage U was measured[27,28]. As temperature dependence of current I=I(l/T) was linear, the activation energy E_a at the given voltage U was determined by Arrhenius equation.

The non-linear current-voltage (CV) characteristics were observed both in the bulk and in the in-plane samples of LB films and it's been typical for low conductive organic solid state (see Figure 5). In case of bulk conductivity at the electric field $\varepsilon > 3 \times 10^6 \mathrm{V/cm}$ (compound **1c**) and $\varepsilon > 1 \times 10^5 \mathrm{V/cm}$ (compound **6**) the superlinear current dependence on electric field appeared. In the Ohmic region the conductivity at room temperature was of the order of $\sigma=1\times10^{-13}$S/cm. In case of the in-plane conductivity the superlinearity of CV characteristics started at lower electric field $\varepsilon > 2 \times 10^2$V/cm as well as the conductivity of material was higher $\sigma=4\times10^{-8}$S/cm for compound **1c** and $\sigma=1\times10^{-10}$ S/cm for compounds **1b** and **6**[16]. In the case of VE films of compound **9**, the value of the in-plane conductivity was less of $\sigma=3\times10^{-12}$S/cm. The values of conductivity as well as its the thermal dependence are typical for molecular insulators. No influence of photoisomerization on electronic properties of LB and VE films was observed.

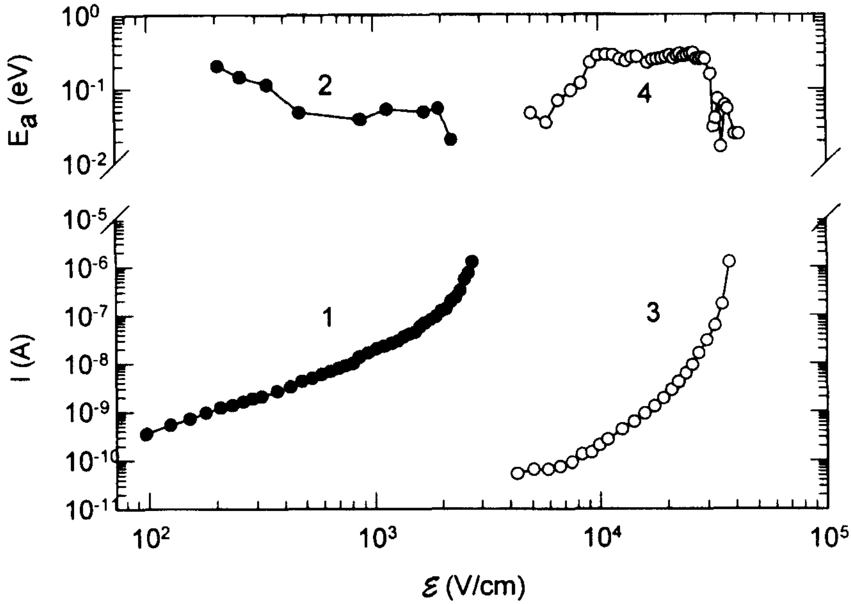


FIGURE 5 Experimental CV-characteristics I(U) and $E_a(\varepsilon)$ dependences of compound **6**. (1), (2) – the in-plane conductivity with coplanar electrode configuration Au/**6**/Au, (40 dips), distance between electrodes 60μm; (3), (4) – the bulk conductivity in "sandwich" type sample Cr/**6**/Al, (16 dips). Temperature range T= 300–240K

8. CONCLUSIONS

In the multilayer films of compounds **1b, 1c, 2b, 3, 10b**, exhibiting molecular area of 23–34Å. no photoisomerization is observed on UV irradiation because of close packing of molecules in monolayer. The optically induced switching effect of the changes of the absorbance and of the surface potential on irradiation with UV and visible light of azobenzene derivatives **6, 9, 11a**, and **11b**, exhibiting molecular area of 77–144Å, is observed. The double-chain structure in the N-alkyl-N-acyl fragment (**11a, 11b**) or the bulky N,N′-dicyclohexyl urea moiety (**6, 9**) might cause looser packing of azobenzene units in the monolayers and, consequently, the molecular reorganization by photoisomerization might proceed more readily. The values of the changes of the absorbance and of the surface potential are dependent on chemical structure of azobenzene derivatives and the kinetics of the switching effect on irradiation with UV and visible light might be described as first-order process.

Contrary to LB films, the photoisomerization process of azobenzene chromophore **9** in VE film does not appear in absorbance measurements while the optically induced switching effect of the surface potential is observed in optically "pretreated" thin films.

The space charge limited current and the anisotropy of electrical conductivity of LB and VE films was observed for all compounds. In Ohmic region of LB films the in-plane conductivity is 3–5 orders higher in that in bulk conductivity. The several sets of charge carrier trapping states were obtained. No photoisomerization effect on electroconductivity is observed.

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