

Structural Rearrangements upon Photoreorientation of Amphiphilic Azobenzene Dyes Organized in Ultrathin Films on Solid Surfaces

Monika Schönhoff,^{†,||} Li Feng Chi,[‡] Harald Fuchs,[‡] and Mathias Lösche^{*,§}

*Institute of Physical Chemistry, Johannes-Gutenberg-Universität Mainz,
D-55099 Mainz, Germany, Institute of Physics, University of Münster,
D-48149 Münster, Germany, and Institute of Experimental Physics I, University of Leipzig,
D-04103 Leipzig, Germany*

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The polarized excitation of azobenzene molecules is frequently used to reorient the chromophores with their dipole transition moments migrating out of the polarization direction of the incident light. Such photoreorientation was shown to occur in molecular interface multilayer films of some amphiphilic azobenzene dyes on solid supports. In this study, the microscopic morphology and morphological changes on irradiation of such systems are investigated with atomic force microscopy (AFM), electron diffraction, and small angle X-ray reflection. It is found that the molecules are locally organized in patches of molecular layers, and AFM indicates that these film patches are crystalline. Macroscopically, freshly prepared films are organized in confluent stacks of these patches, and on irradiation, these structures segregate into confined domains with micron sizes, resembling two-dimensional polycrystals rather than coherent films. Unpolarized irradiation, accompanied with reorientation of the transition moments toward the surface normal, induces a reorganization of the molecules into structures with surface roughness values far above molecular dimensions, which does probably involve material transport over micron distances. Polarized irradiation, leading to in-plane reorientation of the molecules, does not affect the structure so drastically, and it is often difficult to discriminate illuminated from nonilluminated areas in the AFM.

I. Introduction

Photoinduced reorientation and photoelectropoling of azobenzene chromophores^{1–12} and related compounds^{13,14} are well-documented phenomena in thin optical films. In thin liquid–crystalline polymer films, an application potential for optical high density information storage is quite obvious.^{3,4,8,10} In nonlinear optics, chromophores pendant or cross-linked in poled polymer films have been investigated as novel materials with high nonlinearities.^{15,16} In addition it has been shown that the alignment

of the molecules in an adjacent liquid–crystalline phase may be controlled by surface-immobilized chromophores.^{14,17}

We have recently investigated photoelectropoling processes in molecular films of a monomeric hydrophobically substituted azobenzene at solid interfaces¹⁸ and have found that the orientation of the deposited molecules can be reversibly redirected, both in-plane and out-of-plane, such that the macroscopic polarity of the samples can be controlled and that the created structures are stable over long periods in ambient light at room temperature. At the same time we have proposed a model based on the molecular interactions within the films to describe the reorientation process.

In order to achieve structural control over such systems on a molecular length scale, films ought to consist of well-organized molecular strata. Preliminary structural investigations using small angle X-ray reflection indicated, however, that the deposited samples were characterized by a large surface roughness.¹⁸ In this work, we have investigated the morphology of deposited films of such a compound with atomic force microscopy (AFM).

II. Experimental Details

A. Sample Preparation. Figure 1 shows the structure of the hydrophobically substituted amino azobenzene **1**, 4-[[4'-(N-octadecylamino)phenyl]azo]cyanobenzene. (Compound **1** was provided by Dr. S. Palto, Moscow, Russia, and dodecylamine by Dr. G. Decher, Mainz, Germany.) Its absorption spectrum in CHCl₃ solution (0.06 mg/mL \pm 0.126 mmol/L) is shown in Figure 2 and compared with the absorption spectrum of transferred films. Dye layers were prepared in the film balance and transferred in a manner similar to the procedure used for the deposition of a related compound in an earlier work¹⁸ after spreading on pure water (Millipore Milli-Q, resistivity > 18 M Ω cm), the layer was compressed until it appeared optically homogeneous and the pressure just began to rise. It was then

[†] Johannes-Gutenberg-Universität Mainz.

[‡] University of Münster.

[§] University of Leipzig.

^{||} New address: Max-Planck Institute for Colloid and Interface Science, D-12489 Berlin, Germany.

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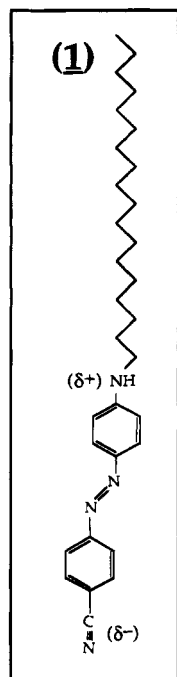


Figure 1. The chemical structure of the azobenzene compound used in this study.

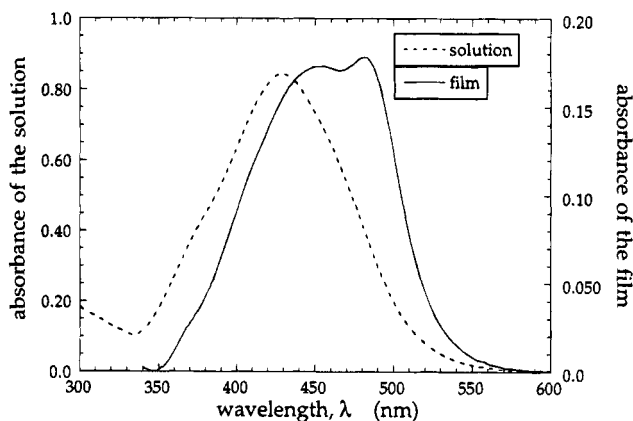


Figure 2. UV/vis absorption spectra of compound 1 in solution (0.06 mg/mL in CHCl_3 ; dashed line) and in a thin film (10 deposited layers) on quartz.

deposited onto the hydrophobic substrate by repeated (typically $10\times$) horizontal transfer. For optical investigations, samples were prepared on glass or quartz substrates cleaned using the RCA protocol and precoated with one monolayer of dodecylamine.¹⁹ The absorption spectrum of the transferred films, 10 layers of 1 on float glass (solid line in Figure 2), shows a pronounced deviation from the solution spectrum (dashed line), indicative of strong aggregation between the chromophores.

Electron microscopy grids were hydrophobized by evaporating ~ 300 Å of carbon. For the preparation of AFM samples and for X-ray measurements, freshly cleaved mica substrates (Mica New York Corp., grade 4, New York, NY) or silicon wafers (Wacker, München, Germany), respectively, were hydrophobized in a film balance with monolayers of dodecylamine, Langmuir–Blodgett (LB) deposited from pure water at a lateral pressure, $\pi_{\text{tr}} \sim 40$ mN/m, prior to the Langmuir–Schaefer transfer of dye films.

B. Instrumental. Samples were characterized with optical microscopy in reflected light (epi-illumination mode) in a Zeiss Axioplan microscope with a 100 W tungsten lamp as the light source. Chromophores in selected areas of samples were reoriented by irradiation in the microscope through a $100\times$ objective lens, using a film polarizer (Zeiss) if applicable. For microlithography, a printed stripe pattern (repeat distance $d \sim 1$ mm) was inserted in the illumination pathway and imaged

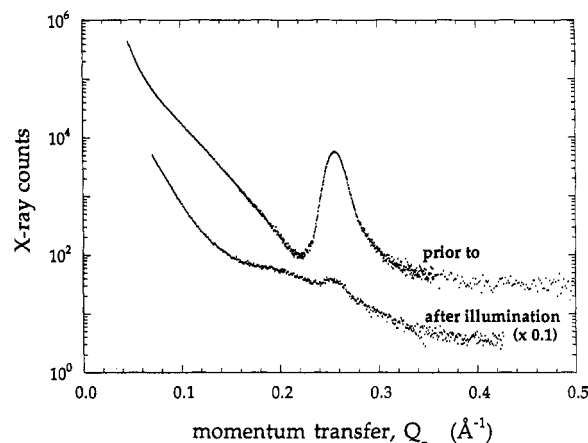


Figure 3. The small angle X-ray reflectogram from thin film samples (10 layers) of compound 1 deposited on a hydrophobized silicon wafer prior to (upper trace) and after (lower trace) unpolarized irradiation (5 min at $I \sim 300$ mW/cm²). The count numbers after irradiation have been divided by 10 for clarity.

onto the focal plane of the objective lens, where it created a pattern of ~ 8.5 μm wide opaque and translucent stripes. The unpolarized irradiation intensity in this mode was $I \sim 300$ mW/cm² in the region of the absorption band (350 nm $< \lambda < 550$ nm), and irradiation times of typically 5 min were used.

Small angle X-ray reflectivity measurements were performed in a modified Siemens D500 diffractometer operated with a $\text{Cu K}\alpha$ source ($\lambda = 1.54$ Å).²⁰

Electron diffraction was carried out in a Philips EM300 operated at 80 kV using field stop diameters in the range of 0.4 – 4 μm .

AFM investigations were conducted in the contact mode using a Park Scientific SFM 2 instrument in air.²¹ For low magnification, a 250 μm scanner was used, and for high-magnification work, a 10 μm scanner was used. Height differences were evaluated under the assumption that different areas on the samples possessed similar material densities, so that compressibility variations of the material are small. Thus, an influence on the apparent topological heights on different regions of the sample was not taken into consideration. The instrument was located in the class 100 clean room of the BASF AG research facility in Ludwigshafen, Germany.

III. Results

A. Layer Structure. Some of the thin film samples deposited on hydrophobized silicon wafers were characterized with small angle X-ray reflectivity measurements. The upper trace in Figure 3 shows a reflectogram from a nonilluminated sample (10 layers) of 1. It exhibits a single broad Bragg reflection around a momentum transfer value (Q_z) of ~ 0.25 Å⁻¹, indicative of an average layer spacing of ~ 24.5 Å. The fact that no Kiessig fringes²² and only one Bragg peak is observed suggests that the film surface is rough, with σ in the range of at least a few nanometers (where σ is the root mean square surface roughness²³). After irradiation, the Bragg peak was greatly reduced (lower trace in Figure 3), indicative of a significant decay of the internal layer structure in the samples.

B. In-Plane Structure on the Macroscopic Length Scale. Reflection microscopy has been used to investigate the photoreorientation effect in samples consisting of 10 layers of 1 on float glass. Figure 4a illustrates different areas on a sample which have been illuminated with different polarization directions as indicated. A first irradiation, on the left hand side ("area I"), was performed

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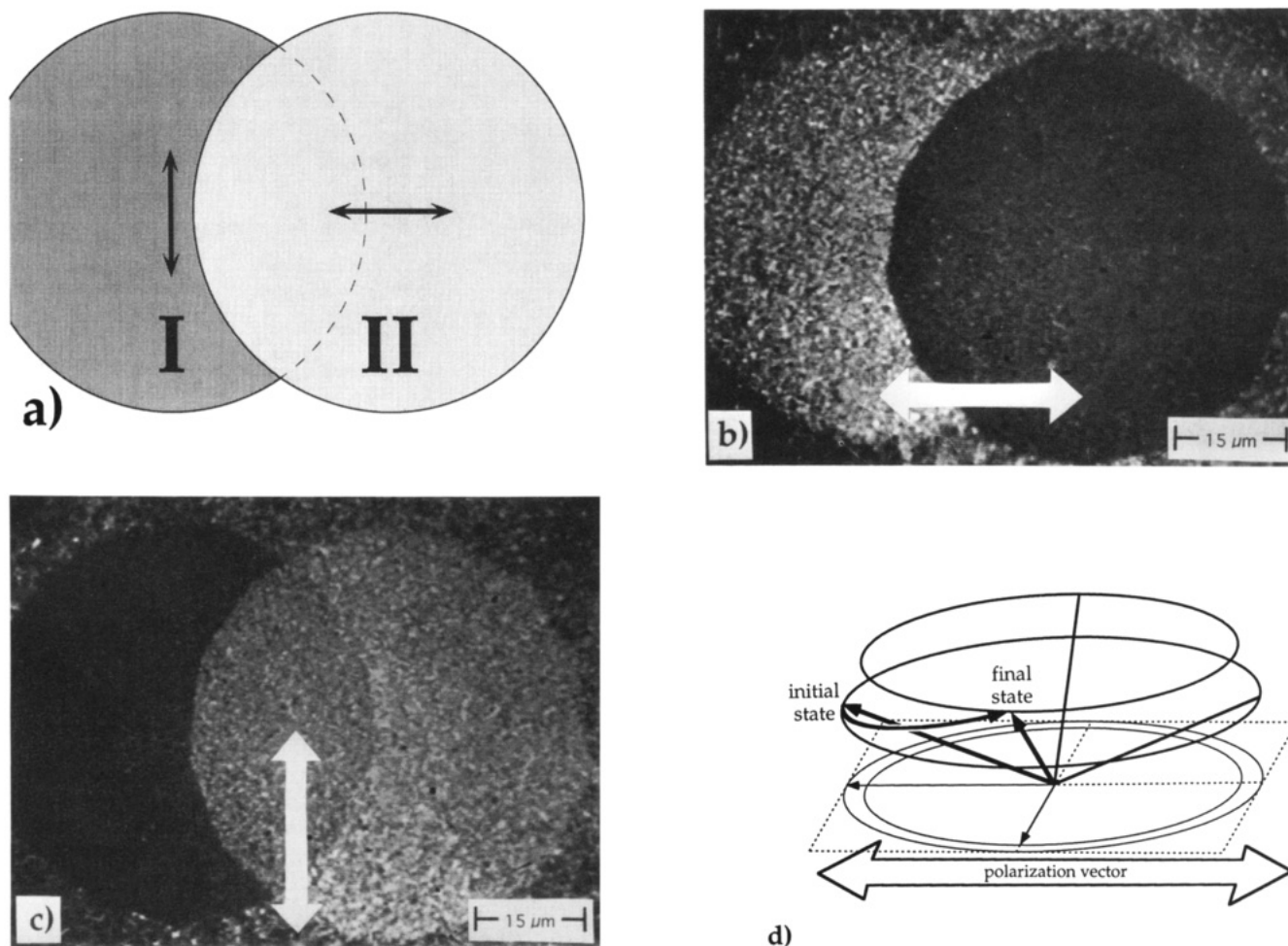


Figure 4. Polarized reflection micrographs of a thin film sample (10 layers) of compound **1** on glass: (a) schematic illustration of different areas on the sample which have been illuminated with linearly polarized light as indicated, (b, c) micrographs observed with different polarizer orientations parallel (b) and perpendicular (c) to the long side of the frames, (d) schematic representation of the light-induced reorientation of molecules within the film.

with the electric field vector of the impinging light oriented vertically, whereas in a second irradiation ("area II"), partially overlapping with the first, the polarization direction was horizontal. For the irradiation and the subsequent observation with linearly polarized light, a microscope was used with the optical axis of its objective lens normal to the sample and its field stop halfway closed. Thus, all polarization directions discussed in the following section lie in the plane of the sample. The local reflected intensity is used as a relative measure of the local absorbance of the sample.

Figure 4b,c show the images observed with polarization directions as indicated. It is immediately recognized, in particular within the nonilluminated areas, e.g., in the upper right corner, that the film shows a grainy structure, with domain sizes close to the diffraction limit, $\approx 1\text{--}2\text{ }\mu\text{m}$ in size. Neighboring domains may show very different reflected intensities in the polarized light. This can be attributed to different average orientations of the projections of the chromophores' long axes on the plane of the sample and indicates that neighboring domains possess uncorrelated director orientations. For simplicity, in the context of molecular orientations, we will use the term "molecules" synonymously for the "chromophores' long axes" in the following discussion. The experimental data can be understood as follows: the average gray levels in the illuminated areas are consistent with a photoinduced rotation of the molecules within the sample plane into directions perpendicular to the respective polarizer orientations, concomitant with a slight reorientation of the

molecules toward the film normal: Figure 4b indicates that the preferred molecular orientation is horizontal after the first irradiation, but vertical after the second in the respective regions, areas I and II. The overlap zone has been depleted of horizontally oriented molecules, as indicated by the fact that there is no distinction between the gray levels there and in area II. This demonstrates that the reorientation is *reversible*. Photoinduced patterns are stable for months in ambient light, which shows that the reoriented states are *persistent*.

The gray level of the overlap zone in Figure 4c, which is intermediate between those of areas I and II, shows that a partial reorientation of the molecules toward the sample normal is superimposed on their in-plane rotation¹⁸ (see Figure 4d). Therefore, the overlap zone and area II are comparably depleted of molecules oriented horizontally, but the concentration of molecules accumulated in the vertical orientation is different, because a partial reorientation of molecules toward the surface normal has occurred in the first irradiation. Hence, the average projection of the molecular orientations on the sample plane was reduced and only a smaller number of molecules was available for reorientation in the second irradiation. That reorientation rather than photodestruction of the chromophores occurs has been demonstrated by measurements of the dichroic absorbance of such films⁹ and by Stark spectroscopy.¹⁸

If illuminated with unpolarized light, the molecular axes evade massively toward the surface normal, as illustrated in Figure 5a, where dark stripes have been induced by an

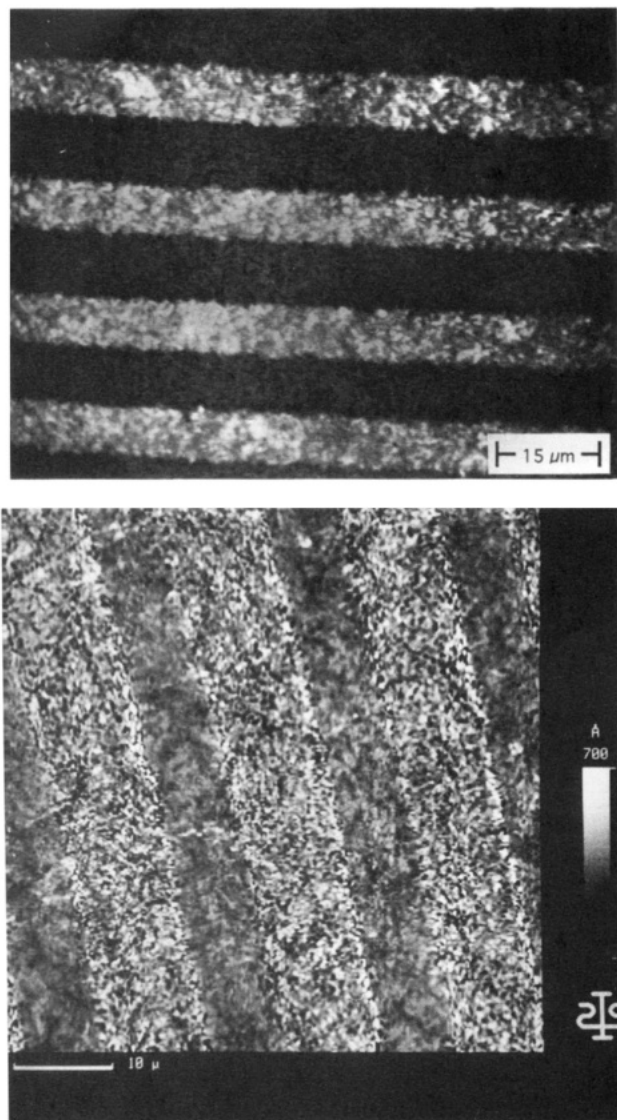


Figure 5. The lithographic stripe pattern formed by irradiation of thin film samples of compound **1** (10 layers) through a mask: (a) unpolarized reflection micrograph after unpolarized irradiation (5 min at 300 mW/cm²) and (b) the AFM image (55 × 55 μm²/700 Å) of a similar sample.

irradiation pattern and are visualized in unpolarized reflected light. The irradiation of selected areas leads to a strong decrease of their reflectance. Again, this is indicative of photoreorientation, rather than photodestruction of the chromophores, as has been shown earlier using Stark spectroscopy.^{1,18}

Figure 5b shows a low-magnification (55 × 55 μm², depth scale 700 Å) AFM image of a similar stripe pattern. The investigation of the sample was performed within 3 h after its preparation and irradiation (5 min at 300 mW/cm²). The pattern is clearly visualized due to an increase in surface roughness in the illuminated areas. The maximum height difference in the sample area shown corresponds to ≥700 Å (within the illuminated areas); within the nonilluminated areas, height differences of ~200 Å are observed, much more than expected for a sample with a well-defined, homogeneous layer structure, for which a total film thickness on the order of 200 Å would be expected.

Similar striped irradiation patterns have been investigated after polarized irradiation at low intensity. Although the structural differences between the two distinct areas are much less pronounced than after nonpolarized irradiation with the same intensity, and in particular the boundaries between the illuminated and the native areas are rather ill-defined, a discrimination

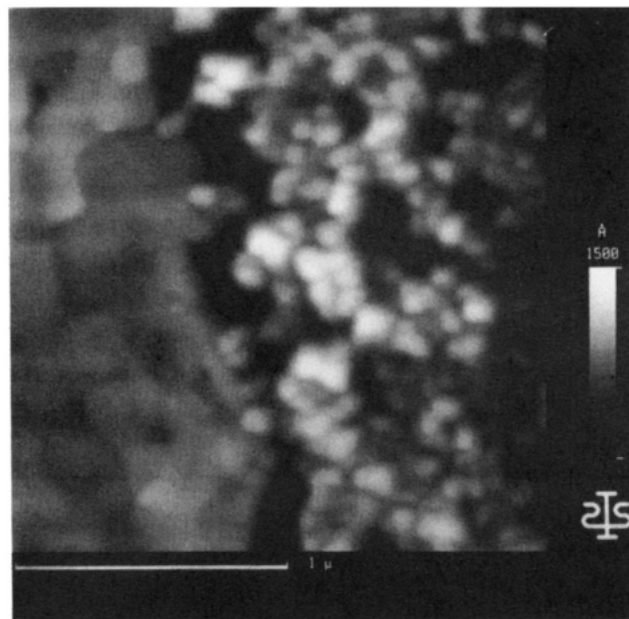


Figure 6. The AFM image (2.1 × 2.1 μm²/1500 Å) of the sample shown in Figure 5b.

in the AFM image is clearly possible, indicating that the in-plane reorientation leads also to an increase in the surface roughness (data not shown).

C. Structure and Structural Transformations on the Mesoscopic Length Scale. Figure 6 displays a close-up AFM view (2.1 × 2.1 μm²) of an area within the sample shown in Figure 5b, where a nonilluminated area (left) borders an area illuminated with unpolarized light (right). The topology on the left hand side is continuous and rather smooth, but not molecularly flat on the micron length scale, although flat areas on a length scale of 100 nm are frequently found. In contrast, the unpolarized irradiation has inferred local melting and has disrupted the film into a large number of islands which extend into the third dimension and possess typical diameters of ~100 nm. These islands may, however, consist of material with internal order on the molecular length scale (see below). Large black patches, preferentially aligned along the borderline between the two distinct areas of the sample, represent presumably surface regions of the dodecylamine-coated mica substrate. Such patches are much less frequently found further away from the borderline, i.e. deeper within the illuminated areas. It is clear that massive mass transport is required to transform the native into the illuminated structure. A further increase in magnification, Figure 7a (0.5 × 0.5 μm²), reveals more clearly that the native topology consists of flat plateaus, piled across each other. These plateaus are molecularly flat and the step height values at their edges are frequently found to be ~25 Å, and multiples thereof. This observation corresponds to the interlayer spacings of ~25 Å observed in the X-ray measurements. The perimeters of the plateaus are rugged and display broken faces along preferred orientations. The maximum height differences within Figure 7a are ~200 Å. In contrast, the height differences in the illuminated areas, as shown in Figure 7b at the same magnification as in Figure 7a, is ~900 Å, and it is clear from the fuzzy spherical shapes shown in that image that the molecular layers have been transformed into three-dimensional structures.

D. Microscopic Structure of Native Sample Areas.

It was not surprising that we were unable to obtain images with molecular resolution within the areas illuminated with unpolarized light. In native sample areas, molecular resolution could be achieved within the molecularly flat plateaus as those shown in Figure 7a. Figure 8 displays



Figure 7. A close-up view ($0.5 \times 0.5 \mu\text{m}^2$) of the native (a; depth scale 200 Å) and the illuminated (b; depth scale 900 Å) areas of the sample shown in Figures 5b and 6.

such a high-magnification image ($120 \times 120 \text{ Å}^2$), taken in air. The sample was inspected 17 d after its preparation. We have not been successful in obtaining similar images from freshly prepared samples, although the flat plateaus are most clearly visualized on such samples. The maximum height difference displayed in Figure 8 is 5 Å. An oblique lattice is recognized as indicated by the two arrows. Whereas long-range positional order is poor, the image shows clearly that long-range orientational order is preserved. The lattice constants of the oblique unit cell are $\sim 8 \times 12 \text{ Å}$. We have also observed smaller lattice constants, $\sim 6 \times 10 \text{ Å}$, on other samples. The origin of the different length scales is not clear yet. It may be due to different molecular packing in different sample areas or to viscoelastic effects, i.e. due to artefacts inferred by the tip in contact mode.

We have tried to obtain more detailed information on the molecular lattice by electron diffraction from films transferred to carbon-coated electron microscopy grids. As shown in Figure 9a (six layers in the film sample), Debye–Scherrer rings were observed from samples prior

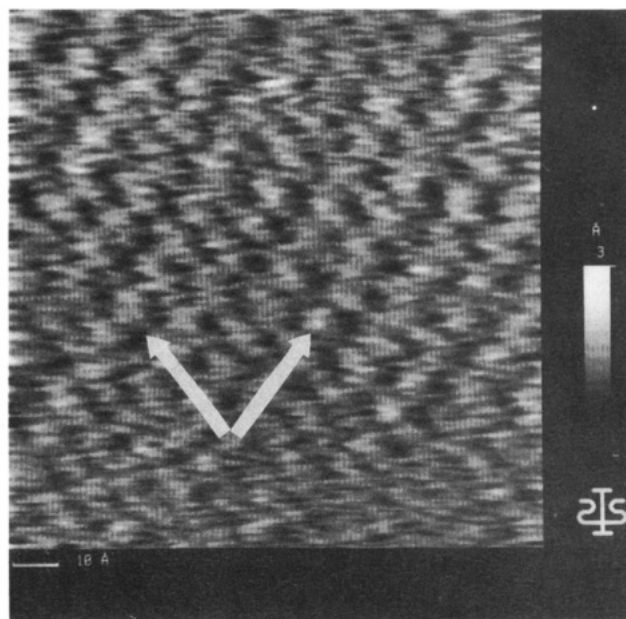


Figure 8. A high-resolution, Fourier-filtered AFM image ($120 \times 120 \text{ Å/5 Å}$) from a nonilluminated sample. A two-dimensional lattice is observed with base vector orientations indicated by the arrows.

to irradiation, indicative of a polycrystalline arrangement of the molecules within the films. These are presumably due to a lateral organization of the chromophores in molecular aggregates within the mesoscopic domains. In contrast, after irradiation (Figure 9b), sharp diffraction spots were found, which could, however, not be attributed to a single periodic structure within the sample. Rather, the spots seemed mostly uncorrelated both in their spacings and relative rotation angles, even when observed with the smallest field stop, and the observed diffraction pattern depended on the position within the sample area. This is consistent with an arrangement of small crystallites at various tilt angles with respect to the electron beam.

We attribute the transition from Debye–Scherrer rings to diffraction spots upon irradiation to a recrystallization of the molecules. Prior to irradiation, the individual layers lie flat and are nearly parallel to the substrate surface, without registry between the layer stacks. After the transformation, there is probably some epitaxial order between the layer fragments, but these fragments may be tilted at a number of different oblique angles with respect to the substrate. The transformed product is thus in a state of larger disorder on a mesoscopic length scale, but the correlation between neighboring chromophores seems intact, consistent with the preservation of the shape of the absorption spectrum upon irradiation.

IV. Discussion

The azobenzene derivatives used in this and a related¹⁸ study show a potential for the preparation of ultrathin films in which the preferential orientation of the constituent molecules, and thus the macroscopic polarity of the sample, can be manipulated by photoelectropoling. However, our structural investigations show clearly that these materials do not readily form molecularly structured films over macroscopic areas. This is presumably due to molecular interactions between the conjugated π systems which induce strong aggregation of the chromophores and overcome the hydrophilic interaction between water and the terminal cyano substituent (or of the sulfonamide group used with a related compound in earlier work). As

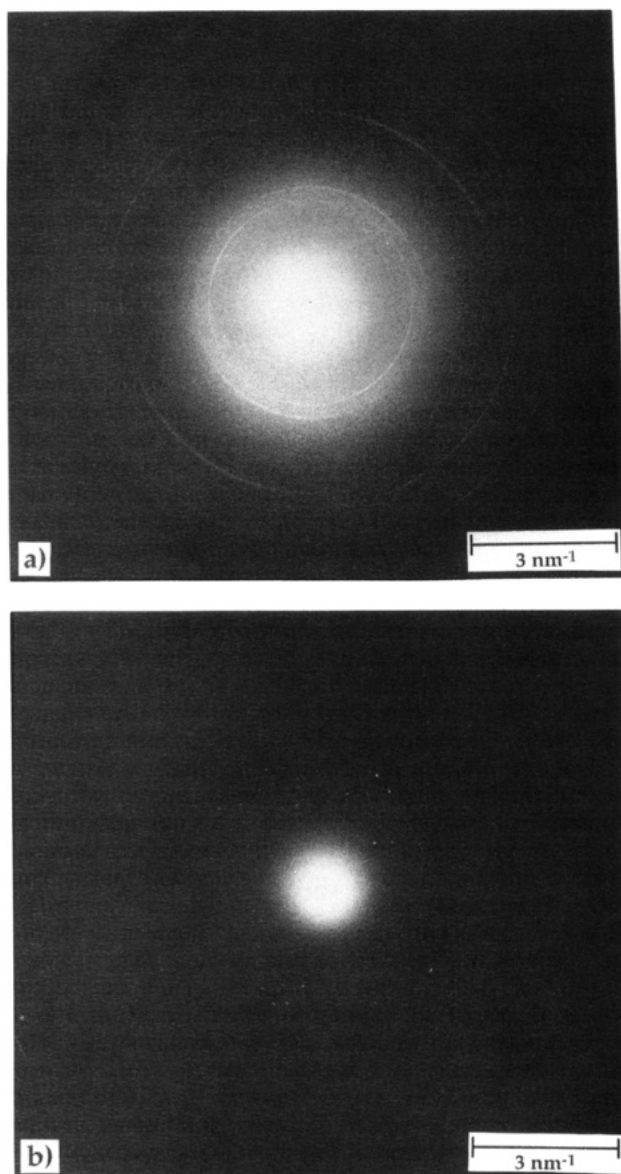


Figure 9. Electron diffraction from thin film samples (6 layers) of compound **1** after transfer to carbon-coated electron microscopy grids: (a) Debye-Scherrer rings observed with a nonilluminated sample, (b) diffraction pattern observed with a sample after unpolarized irradiation. The diffraction pattern in part b depended on the location within the sample from where the diffractograms were taken.

a result, the structures formed on a water surface do not resemble the stable monomolecular films formed by many other conventional amphiphilic compounds. This is indicated by the fact that the azobenzene compounds do not withstand any lateral pressure exceeding a few millinewtons/meter on the film balance and may be compressed to area values well below 20 \AA^2 per molecule, in contradiction with a formation of well-defined monomolecular layers at the surface. Consequently, these compounds cannot be transferred to a solid interface by the conventional LB technique but have to be deposited by horizontally touching the interface film with a hydrophobic substrate. This Langmuir-Schaefer deposition process cannot be expected to lead to comparably ordered structures as the LB deposition, since it would expose a hydrophilic interface to the air after lifting the substrate from the aqueous surface and may thus lead to the formation of molecular double layers, at least on a local basis. Water may be included within the transferred material in sizable amounts between hydrophilic moieties.

On the other hand, replacement of the substituents at the azobenzene core with other moieties which are known

to enable the formation of stable monomolecular films, such as a carboxyl group, leads to a material which has lost its susceptibility for photoreorientation. The fact that the susceptibility for photoreorientation depends so prominently on the substituents has led to the speculation that the reorientation may be inferred by a different mechanism than trans-cis-trans isomerization, since isomerization occurs with all azobenzenes.¹⁸ On the other hand, it is known that the isomerization rate depends on the substituents,²⁶ so that one might speculate that the observed differences between different azobenzenes with respect to their susceptibility for photoreorientation may relate to different time scales for the thermal relaxation from the cis-isomer. Nevertheless, since isomerization rates were reported to be significantly decreased in azobenzenes organized in LB films,⁶ we have suggested a mechanism where the dissipation of excitation energy may increase the rotational mobility of the molecules locally. The drastic structural rearrangements observed in this work after unpolarized irradiation (with a power density that was by far larger than what is required for in-plane reorientation to occur⁹) are indeed indicative of a locally induced recrystallization of the thin film which may be induced either by isomerization reactions or by local heating.

From a quantification of the energy required to control the reorientation process in photoelectropoling experiments, it was inferred that the reorientation is a collective phenomenon and it was proposed that the macroscopic domains which are readily visible in optical microscopy may form the cooperative units. Based on this concept, a quantitative model of the molecular interactions between the molecules within the film was suggested and used in simulations of the reorientation process.^{18,21} The discovery of an ordered phase in high-resolution AFM in the native samples supports such a picture.

Mass transport over micron distances must occur in order to account for the grave structural changes inferred by intense unpolarized irradiation. This is most easily understood if it is assumed that the driving force is the surface free energy and that the rearrangement is facilitated by local melting of the sample. Recrystallization and mass transfer over micron distances have also been documented to occur in LB films almost 50 K below the bulk melting temperature of the constituent material.²⁴

A detailed proposal of the molecular structure of the ordered phase is difficult to obtain on the basis of the high-resolution AFM images. We note that the 2D unit cell parameters observed in the AFM are similar to those of the 3D crystal structure of a similar, but short-chain, compound, 4-[(4'-butoxyphenyl)azo]benzoic acid, projected on one of the planes of the unit cell.²⁵ Whether or not this agreement indicates a similar arrangement of the chromophores is not clear at the moment. We expect, at the least, that it may be possible to limit the number of possible molecular arrangements within the films by rejecting such structures which are incompatible with the AFM results.

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