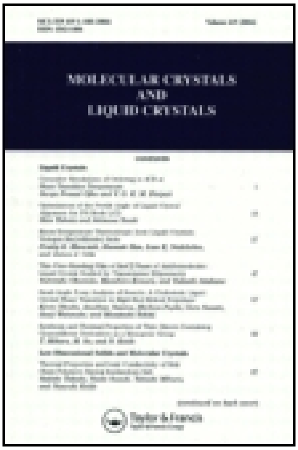

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New Photochromic Materials for Holographic Recording

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New Photochromic Materials for Holographic Recording

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A study of photochromic dihydroindolizines and diarylethylenes was carried out. The photochromism for these molecules is based on an electrocyclic 6π-process. Photochromic films were prepared by embedding these molecules in polythiourethane matrices and their potential as holographic recording material was evaluated.

Keywords: Photochromic materials; holography; information storage

INTRODUCTION

The first hologram was reported by Gabor as early as 1948[1,2]. With the advent of Lasers in 1960, creating 3-dimensional images with holography became practical. Further holographic recording was considerably simplified with the introduction of white light techniques [3,4]. Great advances have been made in the recent past[5].

Recent photophysical developments have caused the need for new holographic materials to become more and more important.

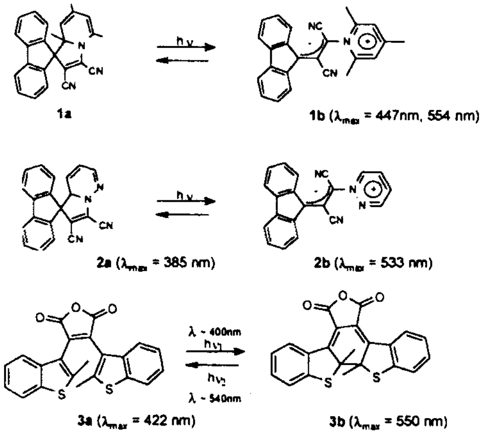
The best suited photochromic systems are photoswitchable molecules in polymeric matrices. Aminopyridines, i.e. polymers with azo-groups in the side chains, are the most often used materials.

PHOTOCHROMIC MATERIALS

In this paper we present a study of photochromic dihydroindolizines[6,7,8,9] (DHI) **1**, **2** and diarylethylenes [10,11,12,13] **3**, which are based on an electrocyclic 6π-process with regard to their photochromism. Polythiourethane-matrices were prepared with these molecules and their potential as holographic material was evaluated.

The following compounds were selected in a study for holography materials.

SCHEME 1



Photochromic dihydroindolizines **1**, **2** and diarylethylenes **3**

EXPERIMENTAL

The photochromic materials **1** - **3** were embedded in a transparent polythiourethane-matrix (PTU). Films of 10, 20, 50 and 100 µm could be obtained by drying a drop of the PTU (prepared from a mixture of diisocyanate and the trithiole using as catalyst dibutyltindichloride let at

20° C (24 h), 60°C, 80°C and 100°C (2 h each)[9] solution between highly transparent glass plates (50 mm · 50 mm · 1,5 mm) using appropiate distance bars. The resulting sample is a pair of glass plates inseparably glued together by the photochromic PTU film. The sample is mechanically rigid and the film is protected from environmental influences such as oxygen.

Samples of 100 μm thickness and concentrations of compound **1** : $0.60 \cdot 10^{-2}$ mol/kg, compound **2** : $0.25 \cdot 10^{-2}$ mol/kg, compound **3** : $1.25 \cdot 10^{-2}$ mol/kg were used. Measurements of photoswitchability and holographic properties were carried out using the setup described in detail in ref. 14.

The optical setup involved an Argon-Ion-Laser working at 514 nm and a filtered Hg-vapor-lamp using the 360 nm line. The sample area chosen had a diameter of ca 8 mm. By using the Laser it was possible to apply an 10 mW/cm^2 „object"-beam and /or a 10 mW/cm^2 „reference" - beam. The object beam was also used to bleach the sample and simultaneously measure the transmission. Object and reference beams applied together recorded a hologram. The reference beam was used to read out a hologram to measure its efficiency. The sample was turned to a position perpendicular to the laser beam during the bleach experiments. For recording holograms, the sample was turned into the correct position. The Hg-lamp was used to colorize the sample with an UV illumination intensity of ca. 2 mW/cm^2. Short time use of the attenuated laser beam with ca. 0.1 mW / cm^2 allowed the measurement of transmission without detectable affection of the sample.

Two Si-detectors with different sensitivities were applied to measure either the transmitted object beam or the weak attenuated beam and the hologram signal. Measurements were monitored by means of computer control to apply the beams with an appropiate sequence and timing.

RESULTS AND DISCUSSION

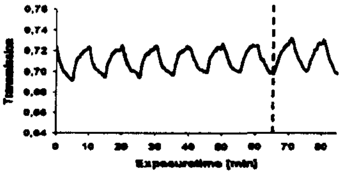
Compound **1** showed only the colored betaine **1b** at room temperature in solution as well in matrices.

The Laser beam leads to a decoloration of the **1b** - matrix. Here the Ar - Ion-Laser induces photodecomposition. **1** is not photoswitchable. Compound **2** can easily be converted to the colored form **2b** using UV light. (The half life of the colored betaine at 25°C in CH_2Cl_2 is $\tau_{1/2}$ = 33 min). A study of the photoreversibility of **2a** ↔ **2b** showed a rather complex behaviour, depending on the employed intensities, temperature and timing. Compound **3** is clearly photoswitchable and photoreversible. The transmission of the colorless probe **2a** at 514 nm was $T_o \sim 73$ % before the experiment ($\phi_R = 0.8$) ; room temperature and room light conditions.

As one can see from figure 1, the transmission drops to T = 69 % within 5 minutes of UV-illumination (360 nm, 2 mW / cm^2) and reaches T = 72.5 % by thermal bleaching during the next 5 minutes. These values were reproduced during 7 cycles of UV-illumination followed by thermal bleaching (left part of figure 1a). Photochemical and thermal bleaching (Laser light : 514 nm; 10 mW/cm^2) during another 5 minutes restores the colorless form to the original transmission value of T ~ 73 %. Again the transmission drops to T = 69 % within 5 minutes of UV-illumination and is restored by photochemical and thermal bleaching (right part of figure 1a).

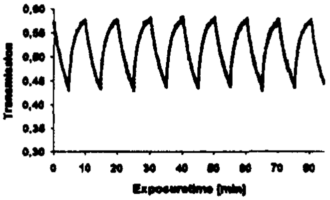
From the small difference in transmission maxima, only a weak contribution for photochemical bleaching **2b** ↔ **2a** can be concluded.

FIGURE 1a



Colorization and bleaching of **2a** ↔ **2b**. Left: 5 min UV irradiation; 5 min thermal bleaching; 7 cycles. Right: 5 min UV irradiation; 5 min Laser irradiation in addition to thermal bleaching; 2 cycles.

FIGURE 1b



Colorization and bleaching of **3a** ↔ **3b**. 5 min UV irradiation; 5 min photochemical bleaching; 8 cycles.

This can be understood because of the small quantum yield ϕ_{back} **2b** ↔**2a** for the photochemical reaction. The value observed is between ϕ_{back} =

photochemical bleaching **2b** ↔ **2a** is inefficient[15,16,17,18] under the conditions employed (see table 1).

Table 1 Quantum yield of photochemical reaction **2b** ↔ **2a**

References	Quantum Yield ϕ_{back}	Temperature °C
C. Schulz[15]	0.003	22
G. Gauglitz[16]	0.002 (±0.10)	20
	0.05 (±0.12)	26
M.Amlung[17]	<0.001	20

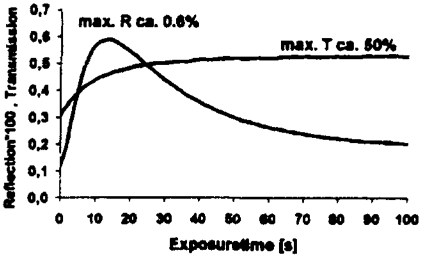
As one can see from figure 1b the molecule **3b** is fully reversibly photochemically bleached to **3a**. The photoreaction **3b** ↔ **3a** shows a very high quantum yield of $\phi_R = 0.21$[19] , therefore a Laser intensity of 1 mW/cm^2 was chosen for the back reaction **3b** ↔ **3a**. At room temperature, there was no thermal bleaching observed. Before the experiment the transmission of the probe **3a** at 514 nm was $T_0 \sim 57$ % (room temperature and room light conditions).

Within 5 minutes of UV-illumination (360 nm, 2mW/cm^2) the transmission drops to T = 43 % and reaches T = 57 % by photochemical bleaching (Laser light: 514 nm; 1 mW/cm^2) during the next 5 minutes. These values were reproduced during 8 cycles of UV-illumination followed by photochemical bleaching.

HOLOGRAM RECORDING

The good characteristics of the system **3a** ↔ **3b** were applied to a study of its holographic characteristics. The setup is designed to record a reflection hologram in a symmetric arrangement with an incident angle mW / cm^2 for both beams. Figure 2 shows an optimal efficiency for the hologram at an exposure time of ca. 13 s corresponding to an exposure of $2 \cdot 10$ mW/cm^2 $\cdot$ sin (65°) $\cdot$ 13 s = ca. 235 mJ. The hologram reaches an efficiency of about 0.6 % which is a reasonable value for absorption holograms.

FIGURE 2



Exposure dependent hologram efficiency of compound **3**-PTU

CONCLUSION

The DHI **1** can not be used as holographic materials because of its irreversibility. **2**-PTU is not efficient enough with regard to the photoswitchability required. Compound **3** in PTU is a promising holographic recording material.

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