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Photochromism of dihydroindolizines Part VIII. First holographic image recording based on di- and tetrahydroindolizines photochromes

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ABSTRACT

The photochromic compounds dihydroindolizine (DHI) and tetrahydroindolizines (THIs) containing dicyano and diesters were prepared via nucleophilic addition of the corresponding heterocyclic bases to spirocyclopropenes. These compounds showed good photochromic reactions both in solution and in polymethylmethacrylate (PMMA)-matrix by photo-irradiation. Holographic recording was measured by employing the thin films of PMMA-DHI and PMMA-THI as recording media. The PMMA-films of DHIs **1–3** were studied with regard to their photochemical switching potential of holograms. In the PMMA-film, these coherent beams were interfering to create a holographic pattern, showing equidistant bright and dark lines. Laser light at 532 nm induced the bleaching processes **1a** → **1** and **2a, 3a** → **2, 3** thus writing the pattern as sinusoidal modulated interference intensity in the photochromic material. The photochemical burning of the interference pattern by the processes **2** → **1a** and **2a, 3a** → **2, 3** is generating the negative holographic pattern in the form of **1** or **3**. The positive recording technique showed that **1**-PMMA produce a hologram grating employing a $\lambda > 400$ nm laser beam with only 1 mW/cm² intensity. This was sufficient to generate a holographic grating due to the high-forward quantum yield for **1** → **1a** of 0.8. The present results indicate that, the UV-laser generated holograms are produced with lower light intensities compared to the vis-laser process in the negative technique. The recording of volume holograms was achieved on the basis of data and information recording system.

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1. Introduction

The demand for higher storage capacity in optical storage is rapidly increasing. As a consequence, many research activities focus on the development of new storage materials [1–6] and innovative technologies [7–9] to simultaneously increase the storage density and data-transfer rates. Holographic recording is regarded as one of the very promising approach to increase the recording density due to its advantages of large capacity and high speed of input and output of information [10]. Holography involves the recording of the interference pattern between a signal beam carrying the information and a reference beam and retrieval of the stored information by illumination of a reference beam. It has been extensively applied to optical data storage because a large amount of data can be stored via various multiplexing method and optical

information can be retrieved with a high-data-transfer rate due to the parallelism of optics [11–14]. Materials are always challenging problem in holographic storage [15–19]. Until recently, materials for practical holographic storage are confined to photorefractive inorganic crystals. However the high cost and inefficient processability limited the applications of inorganic crystals. On the other hand the low cost and ease of fabrication of photorefractive polymeric materials for holographic storage application has attracted and produced many studies in this field. Currently major research groups are focusing on improving on the polymeric materials properties. For successful holographic recording applications, the holographic recording media must satisfy stringent performance criteria, including high-dynamic range, dimensional stability, optical clarity and flatness, rapid response time, millimeter thickness, and non-destructive readout schemes [20].

Generally, there are two main classes of materials used for holographic recording; the first is a photorefractive material and the second is a photosensitive polymerizable acrylic material [21]. Both materials have advantage and disadvantages. For example on the advantage side, the photorefractive material exhibit high-dynamic range and the photosensitive polymer material is sensitive to light

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in the visible spectral region. Slow response time for the photoreflective materials and the need for special fixing information after recording for the photosensitive polymerizable acrylic materials are some of the major disadvantages [10]. Some of these shortcomings can be overcome by using photochromic organic compounds as holographic recording media.

In holographic data-storage systems [22–26] a whole page of information is stored as one interference pattern in a thick photosensitive material. This interference pattern is generated by what so-called object beam (a laser beam on which the information is impregnated by a modulator such as a slide or an LCD image) interferes with the reference beam carrying no information. A large number of interference patterns can be stored in the same site of the medium if these are discernible by direction or site separation. This can be achieved by modifying angle and wavelength of the beam. Such a miniature hologram in the photorefractive material (called: volume hologram), which contains both information on the intensity of both beams and also phase differences [27].

Photochromic organic compounds attracted much attention from both fundamental as well as practical implementations because of their potential applications for optical memory. Diarylethenes, spirobenzopyrans and spirooxazines [28,35] are well-known photochromic materials for photoisomerization reactions and their applications to optical memories switches. The diarylethenes materials have shown to have good thermal stability, fast response, high sensitivity, photon-mode recording and satisfy the requirements of high-density optical memory [28]. It should be noted that the compounds dihydroindolizine (DHIs) and tetrahydroindolizine (THIs) derivatives developed by Dürr in 1979 [28a,29] are the most promising photochromic materials. DHIs and THIs compounds are thermally reversible, fatigue resistant, wide range lifetimes as well as absorption spectra of the colored betaine forms. Nowadays, it is possible to tune the absorption spectra of

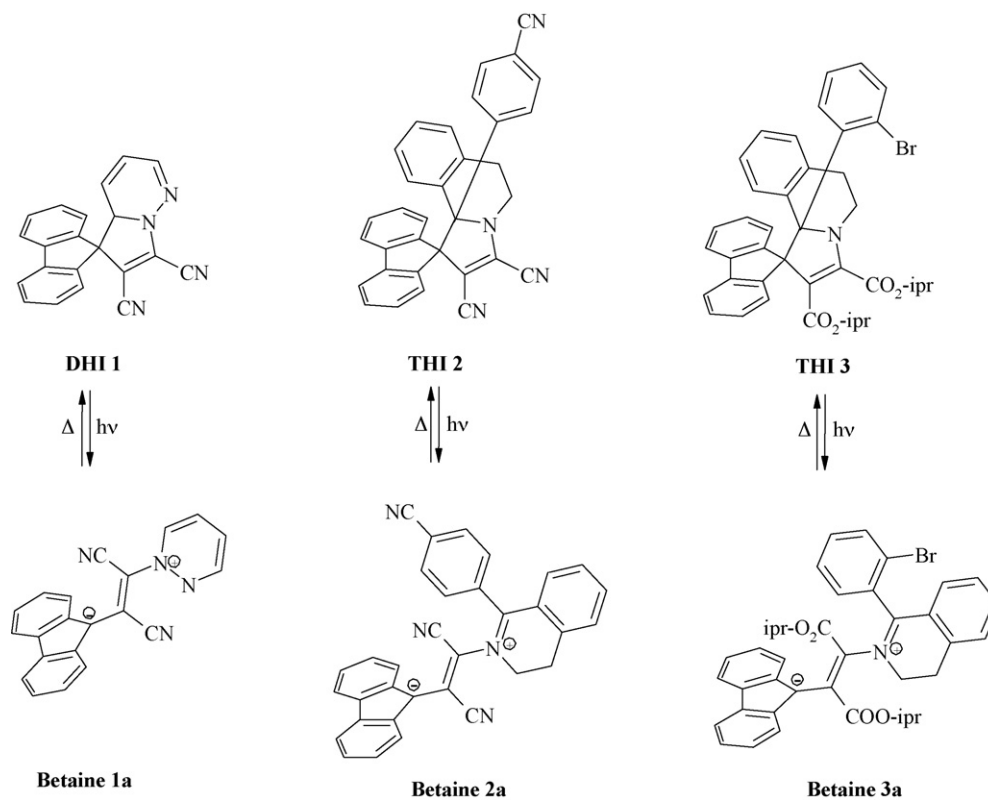
the colored forms, half-lives, photostability, colorability and solvatochromism by changing the substitution in the DHI regions [30–35]. To the best of our knowledge, these advantages only exist in the DHI family.

The present work is a continuation on the preparation and characterization of the dihydroindolizine and tetrahydroindolizine systems. We will focus on: (i) holographic image recoding on DHI (**1**) and THI (**2**, **3**) both having a long-lived colored form in the PMMA-matrix, (ii) the holographic efficiency (recording and read-out) of both di- and tetrahydroindolizines based on data collected on the recording system.

2. Results and discussion

Photochromic DHI and THIs were prepared by the electrophilic addition of dicyano and/or diester fluorenespirocyclopropenes with pyridazine and/or dihydroisoquinolines as heterocyclic base precursors using both the cyclopropene and pyrazole routes [28–35] (Scheme 1). The reaction was run in dry ethereal solution at room temperature under dry nitrogen in the absence of light for 24 h led to the formation of the photochromic di- and tetrahydroindolizines **1–3** in moderate yield. The formation of DHI **1** (Scheme 1) and THIs **2**, **3** proceeded by a cyclopropyl-allylanion rearrangement [29,30]. The dark colored betaines **1a**, **2a**, **3a** underwent 1,5-electrocyclization to give the corresponding DHI **1** and THIs **2**, **3** as shown in Scheme 1.

The photophysical data are collected in Scheme 1 for dihydroindolizines (**1**) [30–35] and the tetrahydroindolizines (**2**, **3**) (see Section 4). In methylene chloride solution, DHI **1** shows a maximum at 410 nm. Irradiating DHI **1** with $\lambda > 400$ nm generates the violet betaine **1a**, $\lambda = 560$ nm [28]. The THI **2** absorb at $\lambda = 360$ nm and THI **3** at 325 nm. Irradiation THI **2** and THI **3** with $\lambda > 400$ nm produces the blue betaines **2a**, **3a** with maxima at 495 and 620 nm



Scheme 1. Photochromic reaction of DHI **1**, THI **2** and THI **3** to the corresponding betaines **1a**, **2a** and **3a**. The quantum yield of the forward photochemical reaction in case of betaine **1a** in PMMA is $\phi_R = 0.8$ and the quantum yield of the thermal 1,5-electrocyclization is $\phi_R = 0.005$.

Table 1
UV-vis absorption DHI **1** and THIs **2** and **3** and their corresponding betaines **1a**, **2a** and **3a** and kinetic data of betaines **1a**, **2a**, and **3a** in CH₂Cl₂ solution and in PMMA-thin film (23 °C, c = 1 × 10⁻⁴ mol/l)

Compound	λ_{\max} DHI in CH ₂ Cl ₂ (nm)	λ_{\max} betaine in CH ₂ Cl ₂ (nm)	$t_{1/2}$ in CH ₂ Cl ₂ (min)	$t_{1/2}$ in PMMA (h)
DHI 1	410	560	56.2	7.5
THI 2	360	495, 620	55	4.8
THI 3	325	484, 659	105.8	3.5

for **2a** and at 484 and 489 nm for **3a**. Thermally, both **1a** and **2a**, **3a** bleach in a 1,5-electrocyclization [30–35] to **1** and **2**, **3**, respectively. The half-lives ($t_{1/2}$) in methylene chloride for **1a** is 56.2 min, for **2a** is 55 min and for **3a** is 105.8 min (Table 1). Similarly, DHI **1** and THIs **2**, **3** also showed good photochromism in the PMMA-matrix and the half-lives increase drastically: $t_{1/2}$: **1a**: 7.5 h; **2a**: 4.75 h; **3a**: 3.5 h.

The photochromic molecules **1**, **2** and **3** were embedded (vide infra) in PMMA-thin films. The DHI- and THIs-doped PMMA-thin films were prepared by dissolving (2 mg) of DHI **1** and THIs **2**, **3** in PMMA-CH₂Cl₂ (10%, w/w, 0.5 ml). The mixture solution of photochromic compounds, polymer matrix in CH₂Cl₂ was then spin coated on a quartz glass substrate and then dried in air and kept in darkness at room temperature. The thickness of the film was approximately ~10 μ m. The sample was irradiated with UV light for 2 min before being recorded. In addition, these molecules were also annealed in polycarbonate and polyvinyl butral matrices but showed inferior properties and were therefore not studied further.

Initially the PMMA-films of **1** and **2**, **3** ($d = 10 \mu$ m) were studied for their potential as photochemical switching holograms. Apparatus for recording simple holographic patterns has been described earlier [10,23]. The experimental setup for holographic recording and readout was presented in Fig. 1. A linearly polarized light generated from an Nd-YAG laser passes through a half-wave plate and a polarized beam splitter. After filtering and collimating, the light is divided into two parts as a reference beam and an object beam. The hologram was recorded by the intersection of the object beam containing the information and the reference beam in the sample film. The hologram images on the sample film were readout by the attenuated reference beam with different angles and the reconstructed hologram images were recorded on a charge-coupled device (CCD) camera. For the analysis of the hologram efficiency which is reading and erasing the optical image in a real-time operation (readout), two basic techniques were employed:

1. *Negative recording technique*: In this technique, the colored form is first generated and then selectively bleached by a laser beam. In this test, the PMMA-matrices of **1** and **2**, **3** were irradiated with an Nd-YAG laser ($\lambda = 435$ nm) until a full coloration of the betaines **1a** and **2a**, **3a** of the whole area was achieved. Then the laser beam ($\lambda = 532$ nm) was separated on a beam splitter

into object and reference beams with equal intensity. In the PMMA-film, these coherent beams were interfering to create a holographic pattern which showed equidistant bright and dark lines. The vis-laser ($\lambda = 532$ nm) induced the bleaching process **1a** → **1** and **2**, **3** → **2a**, **3a**, thus writing the pattern as sinusoidal modulated interference intensity in the photochromic material. The photochemical burning in of the interference pattern by the processes **1a** → **1** and **2a**, **3a** → **2**, **3** is generating the negative holographic pattern in the case of **1** or **2**, **3**.

2. *Positive recording technique*: This recording principle starts from the colorless forms **1–3** creating the hologram as the colored betaine in the PMMA-film. In this case, the interference pattern of the betaine **1a** and **2a**, **3a** was induced by UV-irradiation ($\lambda > 400$ nm) of **1** and **2**, **3** with an N₂ laser.

Fig. 2 represents the transmission curves of the **1**-PMMA and the **2,3**-PMMA-films. Plotting relative transmission versus irradiation time (t) allows a comparison of the holographic growing in of transmission of the three **1**-PMMA- and **2,3**-PMMA-films.

2.1. Back switching

A frequency doubled Nd-YAG laser ($\lambda = 532$ nm) was employed to test the back switching of the betaines **1a** and **2a**, **3a**, which all absorb around this region. The low-quantum yield of **2a**, **3a** versus **1a** renders **2a**, **3a** to be not suitable for holography. Additionally **3a** shows no photoinduced back reaction (vice versa). Doubling the laser intensity for the back switching from 10 to 20 mW/cm² produced the betaines **2a**, **3a** in a lower transmission compared with betaine form of 1-PMMA (Fig. 2). We noted that THI **3** showed only 1/5 of the transmission efficiency of dicyano-pyridazine DHI **1**.

The diester **3a** does not undergo a photochemical back reaction under the same condition. This is in agreement with earlier findings where photoinduced back reaction of ester-betaines was absent [28–34]. The reason for these results lies in the different quantum yields (ϕ_R) for the photochemical back switching. Quantum yields were estimated on the basis of the photons emitted and

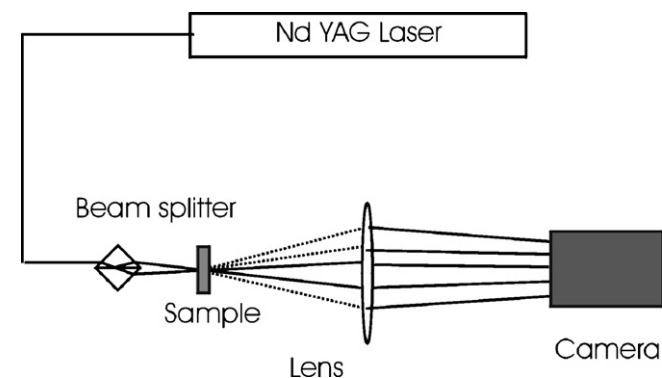


Fig. 1. Schematic diagram of the holographic storage setup.

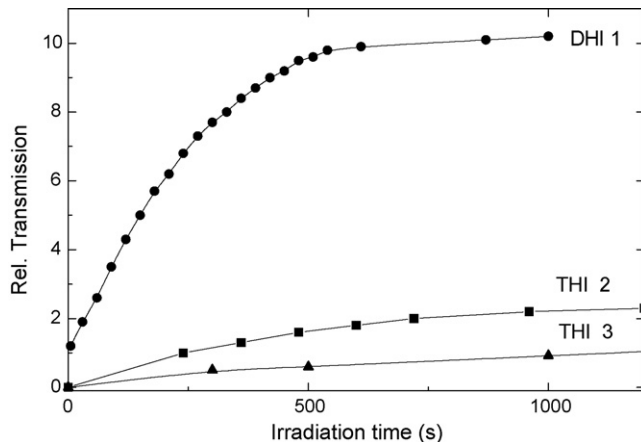


Fig. 2. Relative transmission curves of dicyano-pyridazine DHI **1**, dicyano-THI **2** and diester THI **3** embedding in 1-PMMA-film through irradiation with 355 nm and back reaction by irradiation with 532 nm.

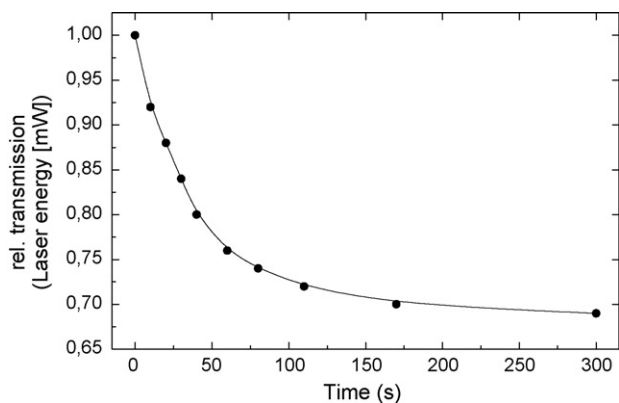


Fig. 3. Development of the transmission signal of **1**-PMMA to **1a**-PMMA as a function of exposure time to UV irradiation at 400 nm in the positive technique studies of **1**-PMMA to produce a hologram grating employing a $\lambda > 400$ nm. The initial laser power of the superimposing recording wave was $P_L = 1.2$ mW/cm² energy and thus tenfold lower than the power necessary for the fading of the betaine **1a** to **1** (negative technique).

the known laser power P_L . For the dicyano-betaine **1a** the ϕ_R value was in the order of 0.005 and for the dicyano-betaine **2a** had much lower value of 0.0001.

2.2. Holograms using the positive technique

1-PMMA was studied using the positive technique to produce a hologram grating employing a $\lambda > 400$ nm laser beam with only 1 mW/cm² energy. This was sufficient to generate a holographic grating due to the high-forward quantum yield for **1** \rightarrow **2** of $\phi_R = 0.8$ [28] (Fig. 3). Thus, the UV-laser generated holograms are produced with lower light intensities compared to the vis-laser process in the negative technique.

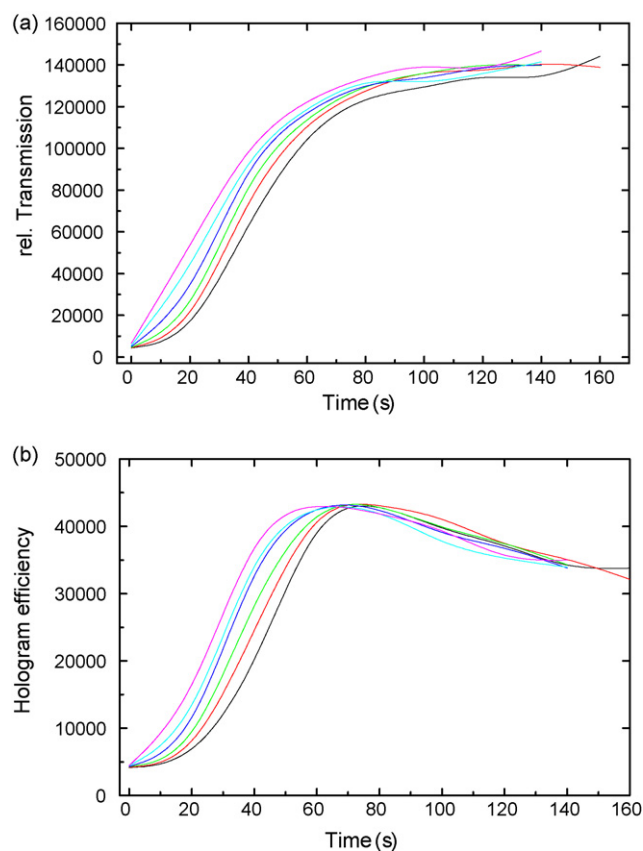


Fig. 6. Relation between the transmission signals (a) and the hologram signals (b) from **2** \rightarrow **1** as function of time at constant laser power $P = 10$ mW/cm² detected with CD camera.

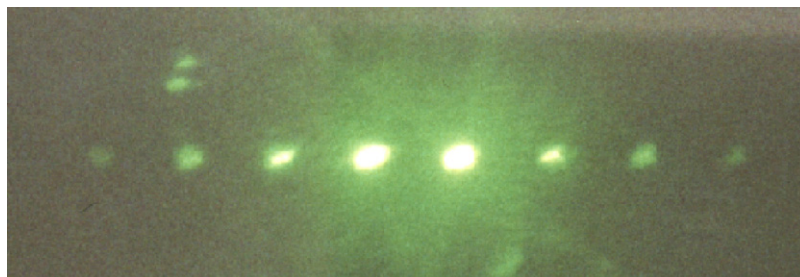


Fig. 4. Storage of symmetric curved picture (**2** to **1**) formed through irradiation with two planer radiation with Nd-YAG lasers at 532 nm of photochromic PMMA-polymer of dicyano-DHI **1**.

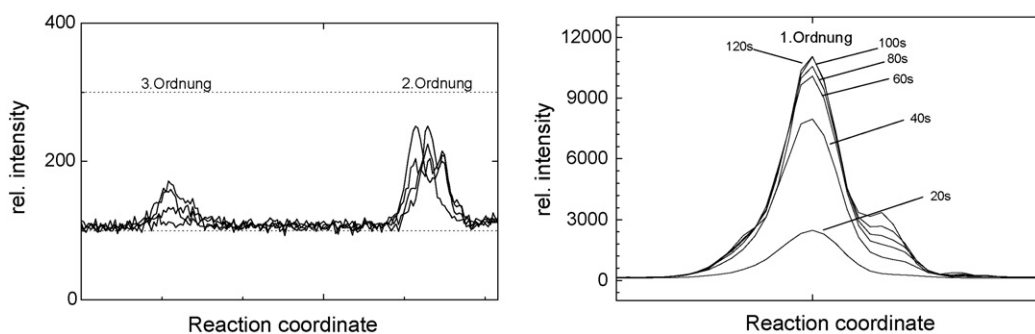


Fig. 5. The different gratings of first, second and third orders of the diffraction reflexes of the holographic grating of the **1**-PMMA recorded with the aid of a CCD camera using a 532 nm laser beam of 10 mW/cm². The transmission signal reaches saturation upon long burning time. Several cycles between punctual photochemical fading and staining were recorded. Ten recorded cycles without substantial loss in transmission demonstrate the good photostability of the DHI **1**-PMMA-system.

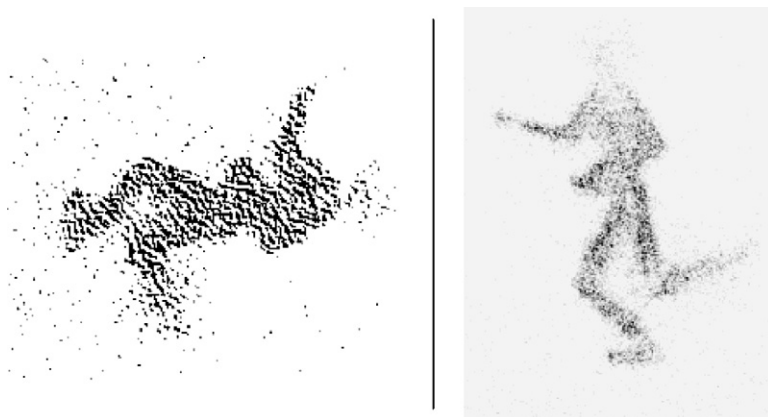


Fig. 7. Two-dimensional holographic image recorded by CDD camera using the photochromic dicyano-DHI **1**-PMMA-layer. A two beam set up was employed and an image (slide: 50 mm image of a runner).

2.3. Holographic studies of dicyano-DHI **1**

Because of its thermal stability and its photoswitchability in both directions, the **1**-PMMA betaine is most suitable for holographic information recording (see Scheme 1). A detailed study revealed that the different experiments with the colored betaine induced high-diffraction efficiency in the photochemical bleaching process. The diffraction grating of first order for **2** appeared only after 5 s of vis-induced bleaching with $\lambda = 532$ nm laser beam after a burning time (bleaching) of 60 s, the second order, after 200 s and the third-order grating increased in intensity (Fig. 4). The colored dicyano-betaine **2a** could produce only a first-order grating under the same conditions.

The diffraction reflexes of the holographic grating of the **1**-PMMA-system were quantified with the aid of a CCD camera. The different gratings of first, second and third orders are shown in Fig. 5. The use of 532 nm laser beam of 10 mW/cm² induced a saturation of the transmission in **1**-PMMA after about 100 s. The maximum hologram efficiency was reached already after 60 s. Longer bleaching times reduce the hologram efficiency slightly.

In dicyano-DHI **1** photochemical burning ($\lambda = 355$ nm) and photochemical bleaching ($\lambda = 532$ nm) could be performed for 10 cycles without noticeable extinction changes. This indicates that the transmission efficiency and the hologram efficiency remained practically unchanged. The latter was however shifted to longer burning times (Fig. 6).

2.4. Two-dimensional holography image recording

The **1**-PMMA-film was investigated with regard to two-dimensional holography using the apparatus already described [10]. Two-beam interference technique is used to examine the film characteristic of holographic recoding. Nd-YAG laser at the wavelength of 532 nm is used to generate laser beam for holographic recoding. The split laser beams in the DHI **1**-PMMA-thin film with a beam-to-beam angle of 60° in air. The beam diameter is 10 μ m and the power of light in each split beam is 10 μ m. The setup used and an image (slide: 50 mm image of a runner) was placed in the object beam which was then focused on a **1**-PMMA-film on a glass plate. The reference beam was brought to interfere on the glass support with the object beam (carrying the image information). Interference of both beams generated an intensity image of the runner, which was stored in the photochromic DHI **1**-PMMA-layer as a hologram (Fig. 7).

This hologram contains all the information of both beams. Therefore, irradiating the hologram of the photochromic probe with the laser beam allows the full image to be reconstructed from

the hologram. Thus, the **1**-PMMA-based hologram behaves as an image recording system. Complex two-dimensional images can be displayed electronically as grey dot images (Fig. 7) or as binary representation of digital data points on a TV screen. The TV screen is excited with a laser beam being impregnated with the image information. The interference with a reference beam can reconstruct the full page, which can be readout by the CCD camera (Fig. 7). For the readout, the reference beam must agree in its properties with the object beam since the smallest deviations in irradiation angle, wavelength or phase render the information reconstruction impossible. Therefore, the enormous potential and large storage capacity of photochromic polymer matrices such as DHI **1**-PMMA make these materials highly interesting candidates for holographic information and data storage. The bleaching process of **1**-PMMA opens up an additional potential for real-time holography.

3. Conclusions

For the first time, evaluation of the potential of photochromic DHI and THIs as an erasable holographic medium by recording, reading and erasing the optical image in a real-time operation has been investigated. For the sake of long term stability and environmental durability of storage devices, DHI **1**-PMMA-thin film showed a rewritable holographic recoding media. The first holographic recording of DHI and THIs were successfully studied. Plotting transmission versus irradiation time (t) allows a comparison of the holographic growing in of transmission of the three **1**-PMMA- and **3a,b**-PMMA-films recording. The UV-laser generated holograms are produced with lower light intensities compared to the vis-laser process in the negative technique. The diffraction grating of first order appeared only after 5 s of vis-induced bleaching with $\lambda = 532$ nm laser beam after a burning time (bleaching) of 60 s, the second order, after 200 s and the third-order grating increased in intensity. The colored dicyano-betaine **1a** could produce only a first-order grating under the same conditions. Interference of both beams generated an intensity image of the runner which was stored in the photochromic **1**-PMMA-layer as a hologram. Low cost and easy information processing of photochromic dihydroindolizine provide a substantial advantage for optical recording and the possibility of material for high-density optical storage may put us one step further toward the use of photochromic materials in various optical applications.

4. Experimental

The solvents used (Aldrich or Merck, spectroscopic grade) were dried, according to standard procedures [36]. Spirocyclopropene

derivatives were obtained via photolysis of the corresponding pyrazoles prepared according to reported procedures. Photolysis was carried out in the photochemical reactor of Schenck [37] made from Pyrex ($\lambda > 290$ nm). The source of irradiation was a high-pressure mercury lamp (Philips HPK 125 W). Solutions to be photolyzed were flushed with dry nitrogen for 30 min before switching on the UV lamp. The progress of the reaction and the purity of the products isolated were monitored using TLC. Separation and purification of all synthesized photochromic materials were carried out using column chromatography (80 cm length \times 2 cm diameter) on silica gel and CH_2Cl_2 as eluent. Melting points were measured on a Gallenkamp- or a Büchi (Smp-20) melting point apparatus.

All NMR spectra were collected on a Bruker DRX 500 spectrometer (500 MHz) in CDCl_3 using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. IR spectra were measured on a Bio-Rad Excalibur series, FTS 3000. Mass spectra were recorded on a Mat-90, FINNIGAN MAT mass spectrometer. Elemental analysis (CHN) was carried out on a LECO CHNS-932-analyzer. UV-spectra were recorded on a FT-UV/VIS HP 6543 computer-spectrometer. The apparatus for recording simple holographic patterns has been described earlier [10,23,27]. The PMMA-films of **1** and **2**, **3** were irradiated with an Nd-YAG laser ($\lambda = 435$ nm) until a full coloration of the betaines **1a** and **2a**, **3a** of the whole area was achieved. Then the laser beam ($\lambda = 532$ nm) was separated on a beam splitter in object and reference beams both having equal intensity. The experimental procedures and full spectroscopic and elemental analysis data of the synthesized and THIs **2**, **3** are listed below.

4.1. Preparation of 2',3'-dicyano-5',6'-dihydro-10'b-(4-cyanoophenyl)-1'H-spiro[fluorene-9,1']-pyrrolo[2,1-a]isoquinoline (**2**)

268 mg (1.0 mmol) of 4,5-dicyano-3H-pyrazole-(3-spiro-9) fluorene and 232 mg (1.0 mmol) of 1-(p-cyano-phenyl)-3,4-dihydroisoquinoline were dissolved in 300 ml absolute diethyl ether, and after 15 min flushing of the solution with N_2 in a circulating photolysis apparatus with a Hg-high-pressure lamp (HPK 125 W) with a Pyrex filter. After several minutes the yellowish solution turned green. The photolysis was finished after 1.5 h, when no N_2 evolution was seen. The reaction procedure was also controlled by the disappearance of dicyano-pyrazole by TLC. Solvent was removed under vacuum and the product **3a** was purified by chromatography on silica gel/methylene chloride. Recrystallization from diethyl ether yielded 200 mg (42.3%) as yellow crystals of **2**, m.p. 277–279 °C. IR: $\nu = 3064$ –3000 (C–H, arom.), 2972, 2860 (C–H, aliph.), 2201 ($\text{C}\equiv\text{N}$), 2227 ($\text{C}\equiv\text{N}$), 1588 ($\text{C}\equiv\text{C}$), 1472, 1426, 1363, 1290, 1119, 946, 843, 740 cm^{-1} . ^1H NMR: $\delta = 2.76$ (dt; $^2J = 16.36$ Hz, $^3J = 4.86$ Hz, 1H, 6'- H_A), 3.18 (m; 1H, 6'- H_A '), 3.71 (m; 1H, 5'- H_B), 4.05 (m; 1H, 5'- H_B '), 5.85 (d; $^3J = 7.96$ Hz, 1H, FI-1 (8H)), 6.24 (d; $^3J = 7.96$ Hz, 1H, 10'-H), 6.71 (t; $^3J = 7.96$ Hz, 1H, 9'-H), 6.89–6.70 (m; 3H, FI-2H, 7H, 1 (8H)), 7.02–7.05 (m; 2H, 7', 8'-H), 7.23 (t; $^3J = 7.52$ Hz, 1H, FI-3 (6H)), 7.20–7.26 (br. signal, 2H, 2'', 6''-H), 7.36 (t; $^3J = 7.52$ Hz, 1H, FI-6 (3H)), 7.62 (d; $^3J = 7.52$ Hz, 1H, FI-4 (5H)), 7.60–7.65 (br. signal, 2H, 3'', 5''-H), 7.73 (d; $^3J = 7.52$ Hz, 1H, FI-5 (4H)). ^{13}C NMR: $\delta = 28.78$ (6'-C), 41.55 (5'-C), 68.99 (spiro-1'(9)-C), 76.56 (10'b-C), 98.43 (3'-CN), 108.86 (2'-CN), 112.47 (4''-CN), 113.25, 117.99, 119.98, 120.67, 124.49, 125.44, 127.17, 127.26, 127.72, 127.95, 128.13, 128.88, 129.05, 129.34, 129.60, 132.17 (q), 132.31 (CH), 133.09 (q), 134.16 (q), 139.54 (q), 140.46 (q), 141.79 (q), 142.54 (q), 145.17 (q). $\text{C}_{33}\text{H}_{20}\text{N}_4$ (472.55); calcd. (%): C 83.88, H 4.27, N 11.86; found (%): C 83.90, H 4.28, N 11.82.

4.2. Diisopropyl-5',6'-dihydro-10'b-(2-bromophenyl)-1'H-spiro[fluorene-9,1']-pyrrolo[2,1-a]isoquinoline-2',3'-dicarboxylate (**3**)

A solution of 1,2-dicarbomethoxycyclopropene-(3-spiro-9)fluorene 362 mg (0.001 mol) and 1-(2-bromophenyl)-3,4-dihydroisoquinoline 268 mg (0.001 mol) in dry ether (50 ml) was stirred at room temperature under dry nitrogen atmosphere with exclusion of light for 168 h (TLC-controlled). Ether was evaporated under reduced pressure and the pure product was separated twice column chromatography on silica gel using CH_2Cl_2 as eluent. Recrystallization from ether–methanol (4:1) afforded 272 mg (42% yield) of **3** as white crystals, m.p. 227–229 °C. UV-vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 324 nm (3.96). ^1H NMR (CDCl_3): $\delta = 7.97$ –7.99 (dd; $J = 1.32$ Hz, $J = 7.96$ Hz, 1H, CH-arom.), 7.63–7.66 (dd; $J = 4.44$ Hz, $J = 7.52$ Hz, 1H, CH-arom.), 7.40–7.44 (t; $J = 6.32$ Hz, 1H, CH-arom.), 7.21–7.29 (m; 3H, CH-arom.), 7.07–7.12 (m; 2H, CH-arom.), 6.85–6.92 (m; 4H, CH-arom.), 6.69–6.77 (m; 1H, CH-arom.), 6.48–6.49 (d; $J = 3.12$ Hz, 2H, CH-arom.), 5.74–5.76 (d; $J = 7.96$ Hz, 1H, CH-arom.), 5.27–5.35 (m; 1H, 3'-CH), 4.31–4.37 (m; 1H, 2'-CH), 3.96–4.00 (m; 1H, 5'- CH_2), 3.41–3.48 (m; 1H, 5'- CH_2), 2.47–2.54 (m; 1H, 6'- CH_2), 2.29–2.38 (m; 1H, 6'- CH_2), 1.37–1.39 (dd; $J = 4.00$ Hz, 6H, 3'- 2CH_3), 0.37–0.39 (t; $J = 1.76$ Hz, 6H, 2'- 2CH_3). ^{13}C NMR (CDCl_3): $\delta = 163.38$ (3'-CO), 163.33 (2'-CO), 148.43, 142.86, 140.90, 133.82, 137.12, 136.11, 135.10, 134.90, 131.43, 129.70, 128.05, 127.65, 127.48, 127.30, 127.04, 126.58, 126.09, 124.79, 122.80, 119.60, 119.28, 80.46 (10b'-C), 70.85 (3'-CH), 68.02 (spiro-C), 65.65 (2'-CH), 41.52 (5'- CH_2), 28.04 (6'- CH_2), 22.18 (3'- CH_3), 22.07 (2'- CH_3).

IR (KBr): $1/\lambda = 3065$ (C–H, arom.), 2866–2987 (C–H, aliph.), 1733 (3'-CO), 1677 (2'-C=O), 1607 (C=C), 1434, 1361, 1312, 1238, 1210, 1164, 1092, 1028, 911, 862, 804, 738, 675 cm^{-1} . $\text{C}_{38}\text{H}_{34}\text{BrNO}_4$ (648.59); calcd. (%): C 70.37, H 5.28, N 2.16; found (%): C 77.35, H 5.31, N 2.22.

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