



## Amide Based Azodyes and their behaviour with Light

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**Abstract.** The light sensitive, amide based azodyes were studied with the UV light illumination of 365 nm. Study revealed that delayed thermal back relaxation is very important for the creation of optical storage devices. It shows almost 22 seconds to convert *E* to *Z* configuration, whereas *Z* to *E* conversion takes about 611 minutes. Presented molecule is having high potential to use in optical storage devices which needs long thermal back relaxation times.

**Keywords.** Azodye, *E-Z* isomerization, Amide, Synthesis and optical storage device.

### 1. INTRODUCTION

A field of research that is growing steadily is that of photo-induced phenomenon, in which the incident light brings about the molecular ordering/disordering of the liquid-crystalline system [1]. First exception to this was reported by S. K. Prasad *et al.*, where they show there exists disorder to order transition [2]. This particular aspect of photonics, in which molecular geometry can be controlled by light, is being proposed as the future technology for optical storage devices [3]. The heart of the phenomenon in such systems is the reversible photo-induced shape transformation of the molecules containing the photo-chromic azo groups [3]. Upon UV irradiation (around 365 nm, corresponding to the  $\pi - \pi^*$  excitation of the azo group), the energetically more stable *E* or trans configuration, with an elongated rod-like molecular form, changes into a bent *Z* or Cis configuration [4].

The reverse transformation can be brought about by illumination with visible light (in the range 400–500 nm, corresponding to the  $n - \pi^*$  band). This latter change can also occur in the dark by a process known as thermal back relaxation. Structure of the molecules seems to be very important to increase their back relaxation time. The present investigation focus on the synthesis and photo switching studies on novel amide based azo-dye molecules which were studied optically using UV light. These molecules relax back extremely slow when light of wavelength 365 nm is shined on them which are necessary condition for the creation of long term optical storage devices.

### 2. EXPERIMENTAL DETAILS

#### 2.1 Synthesis

Chemical structure along with synthetic scheme was given in Figure 1. Ethyl-4-amino benzoate (A) was diazotised by using sodium nitrite and hydrochloric acid. The diazotised nitronium ion was coupled with phenol to produce compound-(B). The terminal hydroxyl group is further etherified by 1-bromo-hexane in presence of base potassium carbonate, potassium iodide was used to increase the rate of reaction. The ether compound-(C) was further hydrolysed using potassium hydroxide/water medium to get compound-(D). Finally, compound-(D) was coupled with 1,6-dihydroxy hexane in presence of DCC/DMAP as coupling agent.



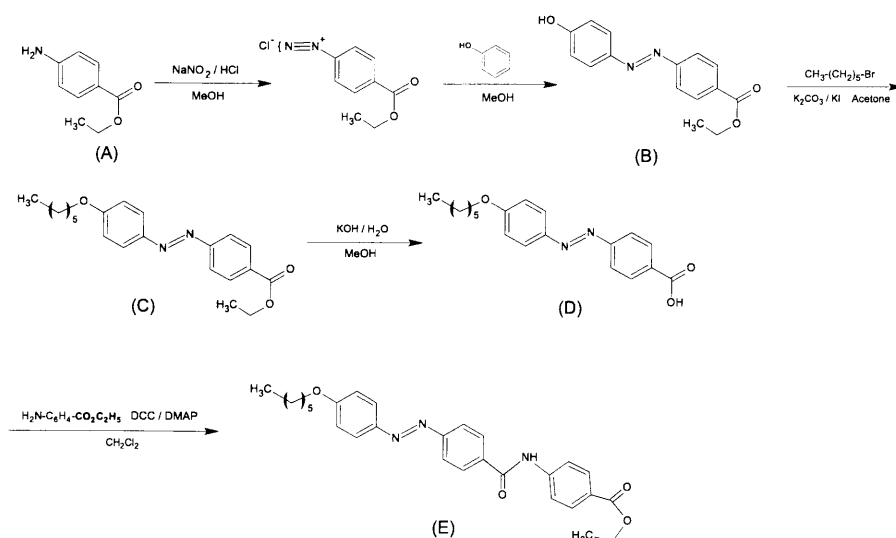


Figure 1. Chemical structure and synthesis scheme of the bent core compound.

The crude product (E) was further purified by column chromatography, followed by recrystallization. Yield is 0.36 g (60%), melting point is 185.5°C.

IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1700 (C = O, aryl ketone), 2852 ( $\text{CH}_2$ ), 2929 ( $\text{CH}_2$ ), 3004 ( $\text{CH}_2$ ), 1092 (C – O, ether), 1640 (C = O, amide), 3326 (N – H, amide, stretch), 1578 (N – H, amide, bent), 1609, 1449 (C = C, aromatic), 1248, 1130, 1092 (C – O), 835 (C – H).  $^1\text{H}$  – NMR (DMSO): 8.55(s, 1H,  $-(\text{CO})\text{NH}-$ ), 8.02(d, 1H,  $J = 8.53$ , Ar-H), 7.90(d, 1H,  $J = 8.30$ , Ar-H), 7.83(d, 1H,  $J = 8.60$ , Ar-H), 7.73(d, 1H,  $J = 8.61$ , Ar-H), 7.64(d, 1H,  $J = 8.31$ , Ar-H), 6.71(d, 1H,  $J = 8.61$ , Ar-H), 2.24(s, 1H,  $-(\text{CO})\text{CH}_3$ ), 4.05(t, 2H,  $J = 7.16$ ,  $-\text{OCH}_2-$ ), 1.88(tt, 2H,  $-\text{CH}_2-$ ), 1.34(tt, 2H,  $-\text{CH}_2-$ ), 1.31(h, 2H,  $-\text{CH}_2-$ ), 1.27(q, 2H,  $-\text{CH}_2-$ ), 0.86(t, 3H,  $-\text{CH}_3$ ). ( $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_3$ , Molecular weight: 443.54).

## 2.2 Sample Preparation

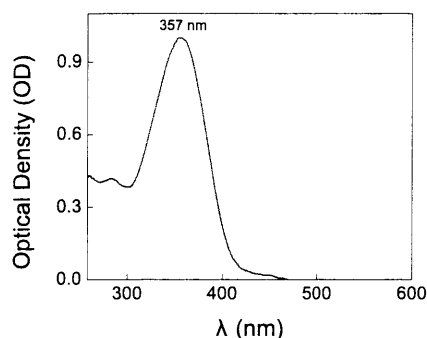
Absorption spectra for photochromic study were recorded using an Ocean Optics HR-2000+ UV-Vis

spectrophotometer. All the solutions along with compound E were prepared using chloroform and measured under air in the dark at room with temperature ( $27 \pm 1^\circ\text{C}$ ) using 1 cm quartz cuvettes. The cuvettes were closed to avoid the evaporation of the solvent and the solutions were not disturbed during the irradiation time. The solutions were irradiated with Hamamatsu light source at 365 nm using suitable filter UG11, and heat filter is inserted to avoid any heating effects. Intensity passing through the filter is measured to be  $5 \text{ mW}/\text{cm}^2$ . Figure 2 shows the UV/Vis absorption spectra of the bent core compound investigated here before illuminating with 365 nm UV light. One can see two peaks from the graph, one corresponds to  $\pi - \pi^*$  at 356 nm and another is  $n - \pi^*$  at 450 nm.

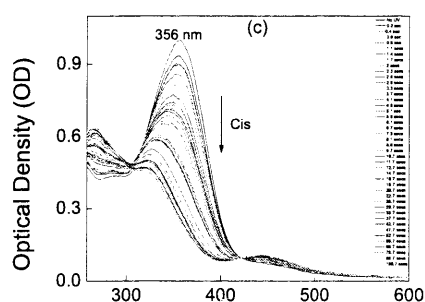
## 3. RESULTS AND DISCUSSION

Photo-switching studies were performed on solutions. It gives an idea of the materials behaviour with respect to UV light and also these results are indispensable for creating optical storage devices. Figure 3 depicts the absorption spectra



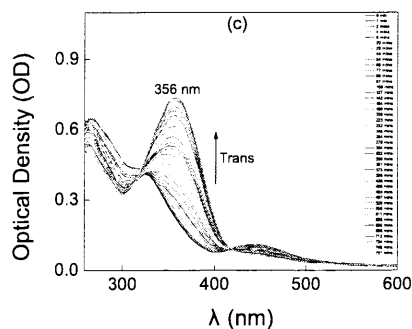


**Figure 2.** UV/vis spectroscopy of *compound E* showing peak wavelength at around 357 nm corresponds to  $\pi - \pi^*$ .



**Figure 3.** Absorption spectra of LGY I with different exposure time of UV light. No UV corresponds to the 0 seconds UV light illumination (absence of UV light).

of *compound E* before and after UV illumination. The absorption spectra of *compound E* showed absorbance maxima 357 nm. The absorption spectra of compound was carried out in chloroform solution having concentration  $C = 1.2 \times 10^{-5}$  mol/L. The strong absorbance in the UV region at 357 nm corresponds to  $\pi - \pi^*$  transition of the *E* isomer (trans isomer) and a very weak absorbance in the visible region around 450 nm represents to  $n - \pi^*$  transition of *Z* isomer (cis isomer). The *compound E* was illuminated with UV light having 365 nm filter at different time intervals and immediately the absorption spectra were recorded. The absorption maximum at 356 nm decreases due to *E/Z* photoisomerization, which leads to *E* isomer transformed to *Z* isomer.



**Figure 4.** Thermal back relaxation processes for the *compound E* shows that to relax from cis to trans takes around 611 minutes. 0 minutes corresponds to the UV off, after illuminating the material for 22 seconds.

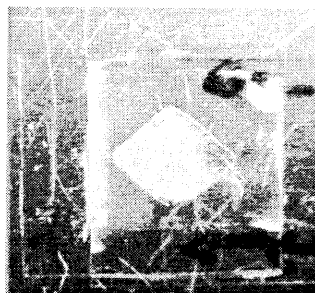
After 22 seconds illumination, there is no change in absorption spectrum confirms the saturation of *E/Z* isomerization process.

Figure 4 shows the thermal back relaxation process where the solution is shined continuously for 22 seconds (photo stationary state) and kept in dark and subsequent time intervals, spectral data were recorded. It is evident from the figure that it took almost 611 minutes (10.18 hours) to relax back to the original trans configuration (*Z - E*).

A possible reason for observing slow thermal back relaxation which is useful for the creation of optical storage devices is may be because of their shape. This argument is supported by the thermal recovery time since it takes longer time to relax after the illumination.

The sample was kept at room temperature and illuminated with UV radiation through a photo masks. The dark regions are the molecules are exposed to UV radiation and the bright regions are where the radiation is masked. An optical storage device is constructed based on these phenomena. Initially material is mixed with liquid crystals (like a guest-host effect) and then suitable mask is inserted. When light of wavelength 365 nm is shined through mask, then one can observe dark regions due to order to disorder transition





**Figure 5.** Demonstration of optical pattern storage capability of the device based on the principle subscribed in this article, it was observed under the crossed polarizers.

(illuminated region) and bright birefringence region (masked region) as shown in Figure 5. This device can stay more than 10 hours due to its high back relaxation time.

#### 4. CONCLUSIONS

Synthesis and photoswitching behaviour of the amide based azo-dyes were presented. Photoswitching behaviour showed very long thermal back relaxation which is quiet useful for the creation of optical storage devices. Optical storage devices

based on presented material is fabricated. Argument based on molecular shape changes were given for the cause of the observed long thermal back relaxation.

#### ACKNOWLEDGEMENTS

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#### References

- [1] M. R. Lutfor, Gurumurthy Hegde, M. M. Yusoff, M. N. A. M. Fazli, H. T. Srinivasa and Sandeep Kumar, New pyrimidine based photoswitchable bent, *New J. Chem.*, 37, 2013, 2460–2467.
- [2] S. K. Prasad, G. G. Nair and Gurumurthy Hegde, Dynamic Self Assembly of the Liquid Crystalline, Smectic A Phase, *Adv. Mater.*, 17, 2005, 2086–2091.
- [3] S. K. Prasad, G. G. Nair, Gurumurthy Hegde, K. L. Sandhya, D. S. Shankar Rao, C. V. Lobo and C. V. Yelamaggad, Photoinduced effects in nematic liquid crystals, *Phase Transitions*, 78, 2005, 443–455.
- [4] M. R. Lutfor, Sandeep Kumar, S. Carsten, I. Gunter, S. Diana and Gurumurthy Hegde, 2009, Synthesis and photoswitching properties of bent-shaped liquid crystals containing azobenzene monomers, *Liquid Crystals*, 36, 2009, 397–407.