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## Synthesis and liquid crystalline behaviour of substituted (E)-phenyl-4-(phenyldiazenyl) benzoate derivatives and their photo switching ability

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### ABSTRACT

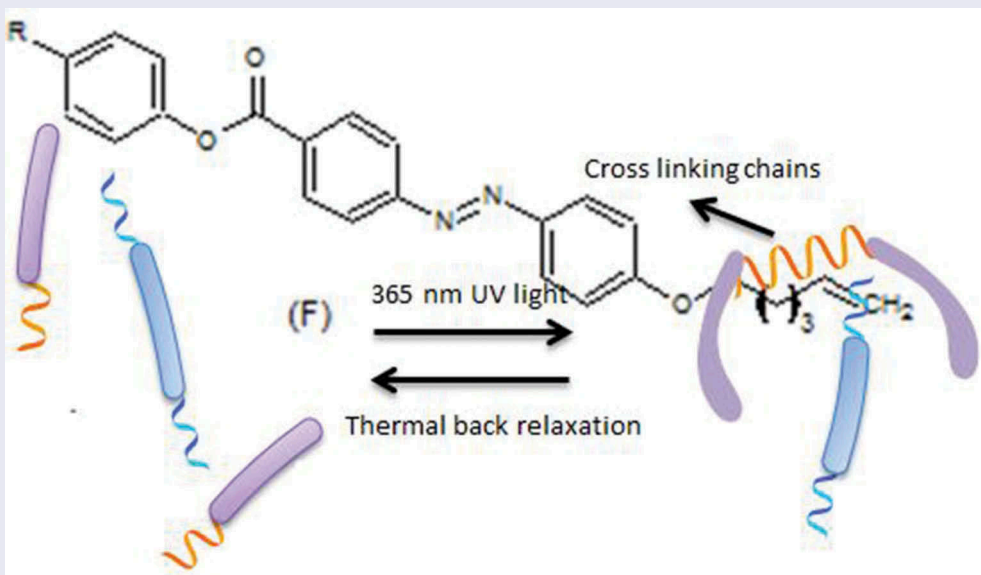
Azobenzene derivatives containing phenyl/4-halogen-phenyl 4-((E)-[4-(pent-4-en-1-yloxy)phenyl] diazenyl)benzoate group with different electronegative substituent (H, F, Cl, Br and I) at other end was synthesised. These azo-based benzoate derivatives have been characterised by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental analyser, POM and UV-Vis spectroscopy. Photosaturation at 358 nm obtained after 82 s of UV irradiation and the longest thermal back relaxation time of 45 h recorded by UV-Vis. The azo derivative could be possible photolock under UV light, as observed by the improved thermal back relaxation time. The resulting photolockable chain of azobenzene might prove valuable in the development of optical device application. These azobenzene moieties also exhibit liquid crystalline behaviour with respect to the halogen substitution as an electron withdrawing group shows that strong structure property relationship exists among them.

### ARTICLE HISTORY

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azobenzene derivatives;  
liquid crystals; storage  
device; thermal back  
relaxation; photolock



## 1. Introduction

Organic photochromic compounds have been attracted a great deal of attention over the last few years due to their potential use in a variety of optical devices employing photoinduced phase transition.[1–6] This process arises from the reversible *trans-cis-trans* photoisomerisation, resulting in the molecular orientation of nematic liquid crystal to higher orientational entropy

(disorder).[7] This allows organic compound containing azo chromophores to be utilised in storing information optically. For optical storage device, azobenzene with long thermal back relaxation is a pre-requisite [8–11], that is, long recovery time from the excited (*cis*) state to the initial (*trans*) state of the system after illumination with UV light of wavelength 365 nm. As to enhance the optical storage features, a

large number of fundamental and technology-driven studies have been done.[12–24] The first possibility in this engineering process lies on the chemical synthesis, where different functional groups can be attached to azobenzene molecules, improving their photochemical characteristic. Photopolymerisation of liquid crystal (LC) has been known for long time.[25–28] It was suggested that the successful photolocking of LC molecules containing polymerised chain provide new strategy for the creation of permanent optical storage devices.[26,27] Orientation of the LC molecules can be varied both locally and optically patterned LC phase can be ‘frozen in’ by subsequent photolocking effect. However, photolocking as an approach to produce long thermal back relaxation have yet to be studied.[29,30] If alkene monomer is substituted by a moiety conducive in the generation of liquid crystal phases, then the resulting polymer may exhibit liquid crystalline phases. It is possible to make azo dye molecules with terminal alkene which comprise an unsaturated carbon-carbon bond to polymerise the molecules. Because illumination with UV light initiates photopolymerisation reactions, each azo monomer will join together at the unsaturated double bond to become long photopolymer chain of azobenzene. Their consequent large molecular mass relative to small molecule compounds produces unique physical properties.

The interest in photopolymerisation of azobenzene molecules also lead us to explore in our study on the effect of electronegativity among the halogene on photopolymerisation activity. Electronegativity is a well-known chemical property that describes the tendency of an atom or a functional group to attract electron (or electron density) toward itself. An atom’s electronegativity is affected by both its atomic number and the distance at which its valence electrons reside from the charged nucleus. The higher the associated electronegativity number, the more an element or compound attracts electron towards it. Hence, it is worth to study the photoswitching behaviour of photopolymerisable azobenzene substituted with different electronegative atoms. These atoms are thought to withdraw electron density from the bonding  $\pi$ -type orbitals of the photochromic azo bridge ( $-N=N-$ ) in the centre of the molecule. A weak  $-N=N-$  bond reduces the barrier for rotation around this bond, which should allow for more efficient inter-conversion since rotation is one of the two pathways (the other one being inversion) for isomerisation. According to Pu et al. [31], the atomic charge on N atom in  $N=N$  bond bearing substituent display no correlation with the electron-withdrawing/donating ability. In fact, the substitutions either by

electron donors or by electron acceptor decrease the electron density on the N atom. It is remarkable that the electron density on the N atom decreases as the atoms electronegativity increases, signifying a considerable dependence on the electronegativity.[32]

In the light of these findings, a series of photolocking azobenzene with different electronegative substituent R (R=F, Cl, Br and I) have been designed and compared them with the one unsubstituted (H atom). The elements F, Cl, Br and I, collectively known as halogen, are very important since one can tailor the materials with changing the electronegative for optical device applications. Their mesogenic behaviour was checked and photolocking with UV light was performed and its effect on thermal back relaxation was investigated.

## 2. Experimental

### 2.1 Sample preparation

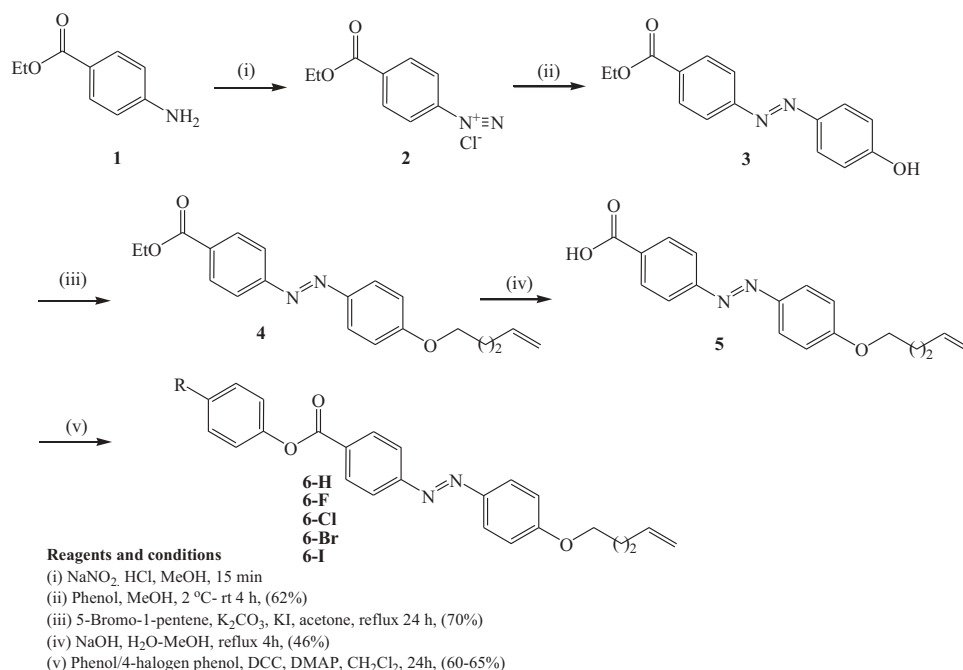
The synthetic strategy is given in Scheme 1 for the preparation of target compounds (**6-H**, **6-F**, **6-Cl**, **6-Br** **6-I**), which contains different halogen substitutions at the para-position with respect to the ester linkage. The structures of all the intermediates and final target molecules confirmed by different spectroscopic methods, *viz* IR spectra recorded using a Perkin Elmer (670) FTIR spectrometer,  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) using Bruker and CHN elemental analyser using Leco & Co.

### 2.2 Investigation of phase behaviour and optical properties

Phase transition of the compounds was studied by using polarising optical microscope. All experiments performed using Olympus BX 51 polarising optical microscope, the polarising optical microscope equipped with a Linkam Hotstage enabling *in situ* high temperature observations under polarised light. Samples were prepared on glass slide and covered with coverslip.

### 2.3 Photoisomerisation studies

Absorption spectra for photoisomerisation studies were recorded using an Ocean Optics HR-2000+ UV-Vis spectrophotometer. Kinetics of both *trans-cis* photoisomerisation and *cis-trans* thermal isomerisation studied for dilute solutions as well as in solid state. All the solution along with the synthesised compounds were



**Scheme 1.** Synthetic scheme of target compounds **6** (H, F, Cl, Br I)

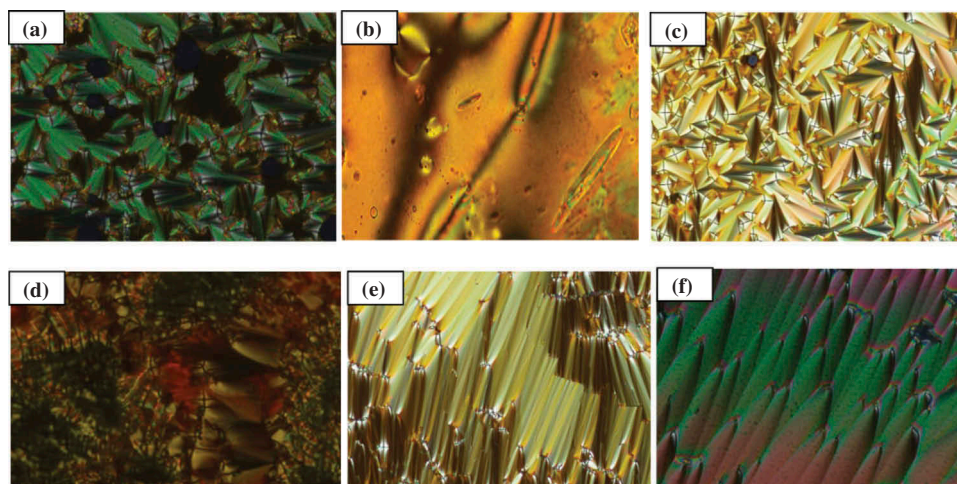
prepared using chloroform and measured under air in the dark at room with temperature ( $27 \pm 1^\circ\text{C}$ ) using 1 cm quartz cuvettes. The cuvettes were closed to avoid evaporation of the solvent and the solutions were not disturbed during the irradiation time. The solutions were irradiated with Hamamatsu light source at 365 nm using suitable filter UG11 and heat filter inserted to avoid any heating effects. Intensity passing through the filter measured to be  $2 \text{ mW/cm}^2$ , which was measured by a broadband power/energy meter model 13PEM001 (MELLES GRIOT) detector and power meter. The spectral data normalised for comparison between the samples. The absorption spectra of the compounds investigated here before and after illuminating with UV light.

### 3. Results and discussion

In order to demonstrate the effect of electronegativity on photocrosslinkable azobenzene, a series of azobenzene with locking alkene synthesised, bearing variable electronegative halogen with crosslinkable 1-pentene attached to its terminal end. Specifically, functionalised halogen with decreasing electronegativity side groups of fluorine (F), Chlorine (Cl), Bromine (Br) and Iodine (I) attached in place of hydrogen (H). The linker 1-pentene moiety was chosen because of the double bond at one end of the molecule capable of undergoing polymerisation.

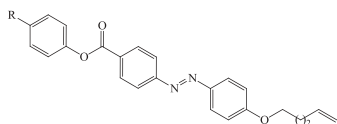
#### 3.1 Mesomorphic properties

All the azobenzene system has alkene terminal group (1-pentene) and the observation with the help of polarising optical microscope exhibits liquid crystalline mesophases. On cooling from its isotropic state, the thread-like appearance which is characteristic of nematic (N) phase evidences for the compounds **6-F**, **6-Cl**, **6-Br** and **6-I** followed by focal conic texture representing smectic A (SmA) phase. However, in the case of **6-H**, where no electron withdrawing group exhibit only SmA phase as shown in Figure 1. Representative microscopic images for various phases are shown in the figure and thread-like behaviour as well as focal conic texture. It is to be noted that inclusion of electron withdrawing group is crucial for obtaining polymorphism liquid crystalline phases, whereas absence of electron withdrawing group exhibit only layered SmA phase. All the compounds (**6-H** to **6-I**) exhibited enantiotropic liquid crystal phase and the transition temperatures are summarised in Table 1. All the compounds were stable even at high clearing temperatures, especially the compound **6-Cl** and **6-Br** on periodic POM observation. Terminal substituted halogens are more polarisable and larger in size favourable for space filling concept giving rise to layered arrangement, the driving force for the formation of layered smectic phase is considered to be specific anisotropic interaction between unlike mesogenic units. [33–36] The melting temperature ( $T_m$ ) of the series



**Figure 1.** (colour online) Microphotographs (crossed polariser) of the textures observed at room temperature for the dyes at different temperature in the cooling cycles from isotropic phase of the compounds 6H-6I. Focal conic images represents smectic A (SmA) phase and thread-like appearance is for the nematic (N) phases. Focal conic texture of SmA phase for 6-H at 132°C (a), thread-like appearance represents nematic phase for 6-F at 200°C (b), SmA phase for 6-F at 152°C (c), SmA phase for 6-Cl at 155°C (d), SmA phase for 6-Br at 172°C, SmA phase for 6-I at 180°C (f)

**Table 1.** Phase transition temperature (°C) on both heating and cooling cycles of all the compounds as observed in OPM



Compounds	-R	Cr	OPM observation					Iso
			Heating Cooling	SmA	Heating Cooling	N	Heating Cooling	
6-H	H	*	129 109	*		-	203 201	*
6-F	F	*	131 98	*	185 184	*	205 203	*
6-Cl	Cl	*	143 117	*	201 199	*	257 256	*
6-Br	Br	*	153 121	*	203 201	*	254 253	*
6-I	I	*	160 130	*	205 204	*	238 237	*

Cr: crystalline phase; SmA: smectic A phase; N: nematic phase; Iso: isotropic phase, (\*: phase exists; - : phase does not exist).

observed in the range of 95–160°C and clearing POM observation revealed that the compounds **6-F** to **6-I** show N and SmA phases, whereas **6-H** exhibit only SmA phase. It is evident from the [Table 1](#) that electron withdrawing halogen are crucial for polymeric behaviour.

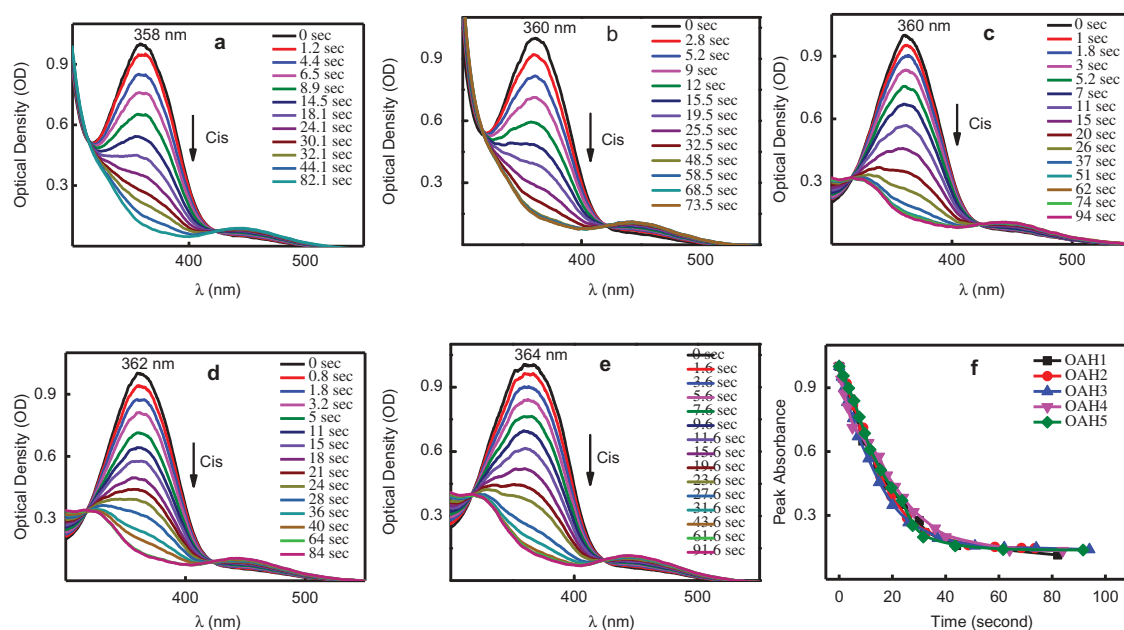
### 3.2 Photoisomerisation studies

Before UV irradiation, all compounds in solution featured absorption band at wavelength between 358–364 nm and a relatively low absorption around

450 nm. The former band correspond to  $S_2 \leftarrow S_0$  transition absorbs at ~360 nm (corresponds to a symmetry-allowed  $\pi-\pi^*$  transition) whereas the latter band correspond to  $S_1 \leftarrow S_0$  transition appears as a weak band at ~450 nm (correspond to a symmetry-forbidden  $n-\pi^*$  transition).<sup>[37–40]</sup> The *trans* isomer of **6-H** has absorption maxima at 358 nm and there are no significant changes in the absorption spectra of halogen substituted compounds which are from the same group-17 of periodic table. This is contrary to our previous publication on fluorine addition into azobenzene-based ester, as there is a significant bathochromic shift as more number of fluorine atoms is added into the structure.<sup>[10,11]</sup>

Upon UV illumination, peak absorption at UV region (correspond to  $\pi-\pi^*$  electron transition) decreased due to *trans* to *cis* isomer conversion, followed by slight increase in the peak around 450 nm (correspond to  $n-\pi^*$  electron transition). This phenomenon arises from the functionality of photochromic properties of azo group. All the compounds (**6-H** to **6-I**) undergo *trans*-to-*cis* photoisomerisation following the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  excitation.<sup>[34,35]</sup> [Figure 2](#) illustrates the spectral changes for compound **6-H**, **6-F**, **6-Cl**, **6-Br** and **6-I** monitored by UV-Vis during UV exposure.

The results reveal that **6-F** took the shortest time for *trans*-to-*cis* conversion, which is 73 s whereas **6-I** took the longest time, which is 91 s. This spectral data confirmed the photoreaction, wherein the photoisomerisation process lead to a photostationary state. At this state, the *cis-trans* isomers ratio is dependent on the



**Figure 2.** (colour online) Changes of absorption spectra during UV exposure; (a) -6-H, (b) -6-F, (c) -6-Cl, (d) -6-Br, (e) -6-I, (f) the plot of peak absorbance vs. time extracted from a, b, c, d and e

wavelength used.[41] As, all the compounds show maximum absorption in the UV region, they give more than 85% of conversion efficiency after exposure to UV light at wavelength 365 nm. Consider the case of **6-H**, for example, 88% of the sample (in solution) have been converted to *cis* isomer after exposure to UV radiation for 82 s. The conversion efficiency (*CE*) (it is also called as extent of photoisomerisation) of the *trans-cis* photoisomerisation is estimated from Equation (1).[42,43]

$$CE = \frac{A(t_0) - A(t_{\infty})}{A(t_0)} \times 100\% \quad (1)$$

here  $A(t_0)$  is absorbance before UV and  $A(t_{\infty})$  is absorbance after UV. Table 2 shows the summary of time taken for the five azo derivatives for *trans-cis* photoisomerisation with their calculated conversion efficiency. Detailed kinetic description about first-order plots were given in later section of the manuscript.

The reverse transformation from *cis* to *trans* can be brought about by two methods: first method is by

**Table 2.** Time taken for the azo derivatives for *E-Z* and *Z-E* isomerisation with their calculated conversion efficiency

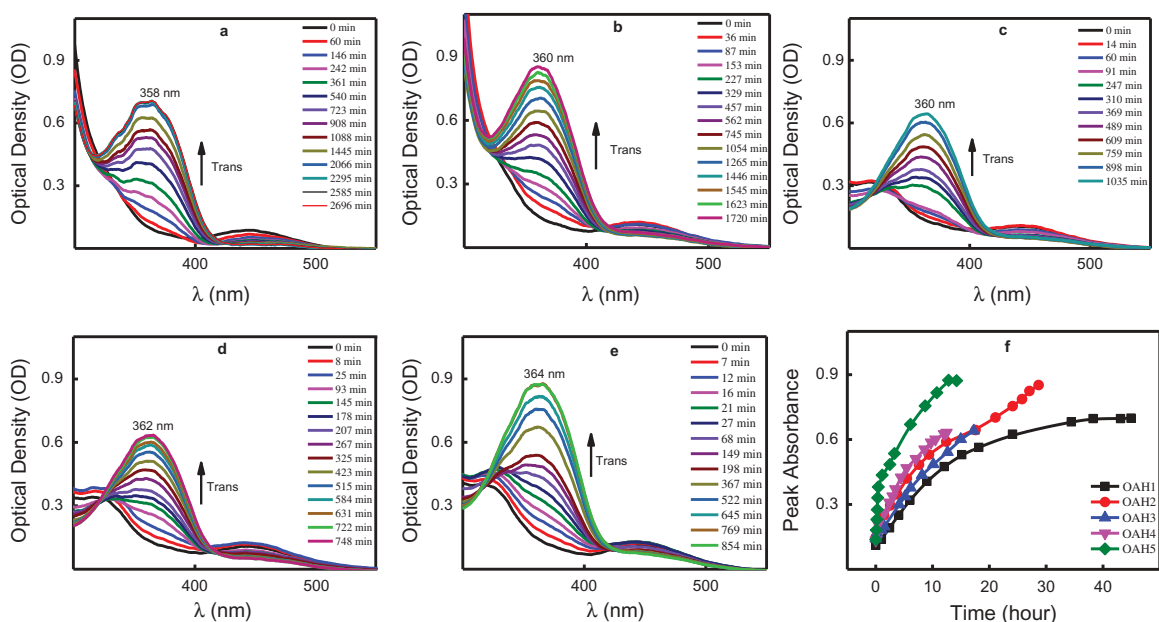
Designation	<i>E-Z</i> (Time) (s)	<i>Z-E</i> (Time) (h)	<i>CE</i> (%)
F <sub>1</sub>	82	45	88.6
F <sub>2</sub>	73	28	85.4
F <sub>3</sub>	94	17	86
F <sub>4</sub>	84	12	86.6
F <sub>5</sub>	91	14	86.2

keeping the solution in the dark to allow thermal back relaxation process to take place and the other method is by shining white light of higher wavelength.[37] To observe the thermal back relaxation process after molecules attaining photosaturation state, samples are left in the dark to allow *cis-trans* transformation. The effect of structural modification can be observed in their thermal back relaxation time. Figure 3 shows the spectral changes of **6-H** to **6-I** during thermal back relaxation process where the *cis* isomers return to *trans*. Among all, **6-H** shows the longest thermal back relaxation time of 45 h.

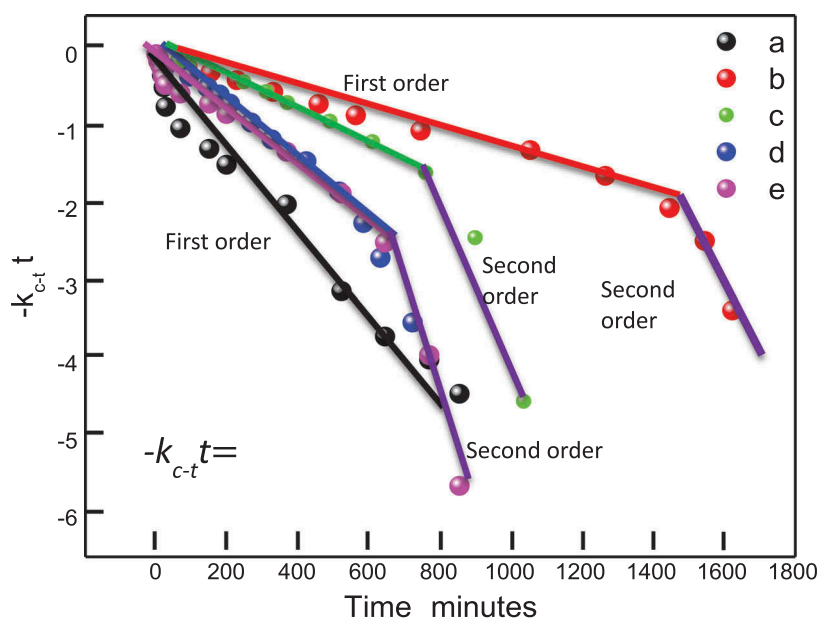
For *trans-cis-trans* photoisomerisation, it is necessary to measure first-order plot for chemical reaction. [44] Figure 4 shows the first-order plot which is measured by fitting the experimental data to the Equation (2) [39] at room temperature 25°C.

$$\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_0} = -k_{c-t}t \quad (2)$$

where  $A_t$ ,  $A_0$ ,  $A_{\infty}$  are the absorbance at peak wavelength at time  $t$ , time zero and infinite time, respectively. The reaction was first-order in the time region indicated. But, it is also observed that it will deviate from the first-order curve at latter part of the reaction, mainly due to the long thermal back relaxation might affected the experimental temperature conditions (since this experiment is carried out in solution). Here, one can mainly observe the change in back relaxation time with respect to chemical structures.



**Figure 3.** Changes of absorption spectra during thermal back relaxation; (a) – 6-H, (b) – 6-F, (c) – 6-Cl, (d) – 6-Br, (e) – 6-I, (f) the plot of peak absorbance vs. time extracted from a, b, c, d and e

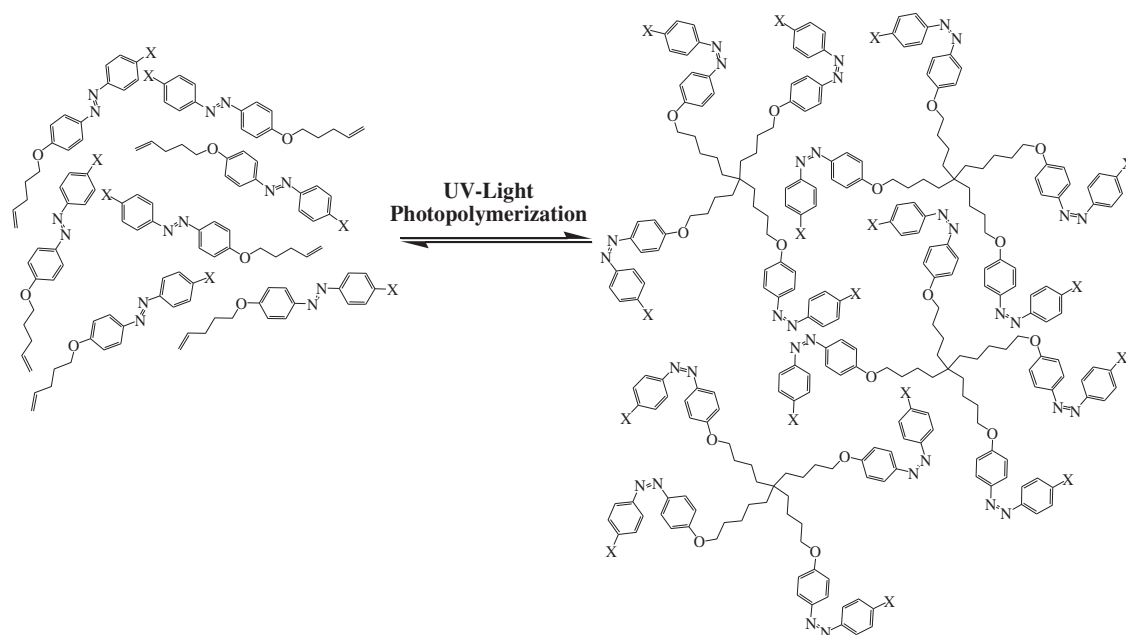


**Figure 4.** First-order plots for Z-E thermal isomerisation for reported compounds (a) – 6-H, (b) – 6-F, (c) – 6-Cl, (d) – 6-Br, (e) – 6-I, (f) measured at room temperature 25°C

This is also the best example to show the kinetic description of the compounds.

The long thermal back relaxation might be due to photolocking of 1-pentene terminal moiety, wherein, this moiety has the ability to undergo efficient photo-initiated polymerisation.[45] In addition to that, having a double bond at the alpha ( $\alpha$ ) position enhances the reactivity of azo derivative.[46] As a consequence, it absorbs the UV energy and initiates photopolymerisation in 6-H through formation of intermolecular

lockable chains by the UV light at wavelength 365 nm. In most cases, the photopolymerisation involve the production of singlet and triplet in excited state [45,47–49], which then react with other 1-pentene terminal moiety nearby. The photolocking effect subsequently creates an entangled polymeric network which restricts the *cis* isomers to go back to the original *trans* configuration. Thus, the geometrical restrictions should be a function of the crosslink moiety as shown in the proposed model in Figure 5.



**Figure 5.** Photoinduced polymerisation model showing the photolocking effect observed in the molecules (6-H, 6-F, 6-Cl, 6-Br, 6-I) in solution. Such system gives a long thermal back relaxation due to locking effects

With increase in atomic number down the group-17, the electronegativity decrease from F(4.0) > Cl(3.0) > Br(2.8) > I(2.5). **6-F** characterised by fluorine substituent, the most electronegative group of all elements, gave 28.66 h of thermal back relaxation. One can see from Figure 3(b–e), as the electronegativity of halogen increased, the thermal back relaxation extended significantly from 14.23 h to 28.66 h. Interestingly, these results are lower considerably in comparison to that of **6-H**, indicating that the photolocking behaviour interacts with the different electronegativity of group-17 elements. These might be the consequence of changes in the electron distribution on the N atom bearing halogen substituent group.[32] Needless to say, the photolocking is a useful method to improve the thermal back relaxation in azobenzene molecules. However, substitution of electronegative element as functional group does not extend thermal back relaxation in azobenzene with photocrosslinkable 1-pentene.

As soon as UV light of wavelength 365 nm is shined on them, energetically stable *trans* molecules convert to *cis* molecules, in other words system goes from order to disorder state.[8–11] Although exact reason is not much clear but we speculate that, here, with the effect of UV light, there might be the possibility of partial photo-locking effect as shown (Figure 6). Reverse phenomena of bringing them back to the original *trans* configuration is not easy and it takes very long time may be due to the mechanism of locking. Further investigation in this direction is in progress and will be reported elsewhere.

#### 4. Conclusions

In conclusion, the nature of 1-pentene terminal group has a strong influence on the thermal back relaxation process. Electron withdrawing groups will help to induce liquid crystallinity. Both photochromic azo group and electronegative substituents found to induce strong photoisomerisation. This study gives an important aspect to utilise the photochemically induced process for long thermal back relaxation, mainly due to 1-pentene terminal group appears to photo induce through the formation of intermolecular cross-linked chains. Further, on fine tuning the terminal cross-linker tail, one can able to get permanent locking effect in which optical storage devices can last longer.

#### 5. Experimental section

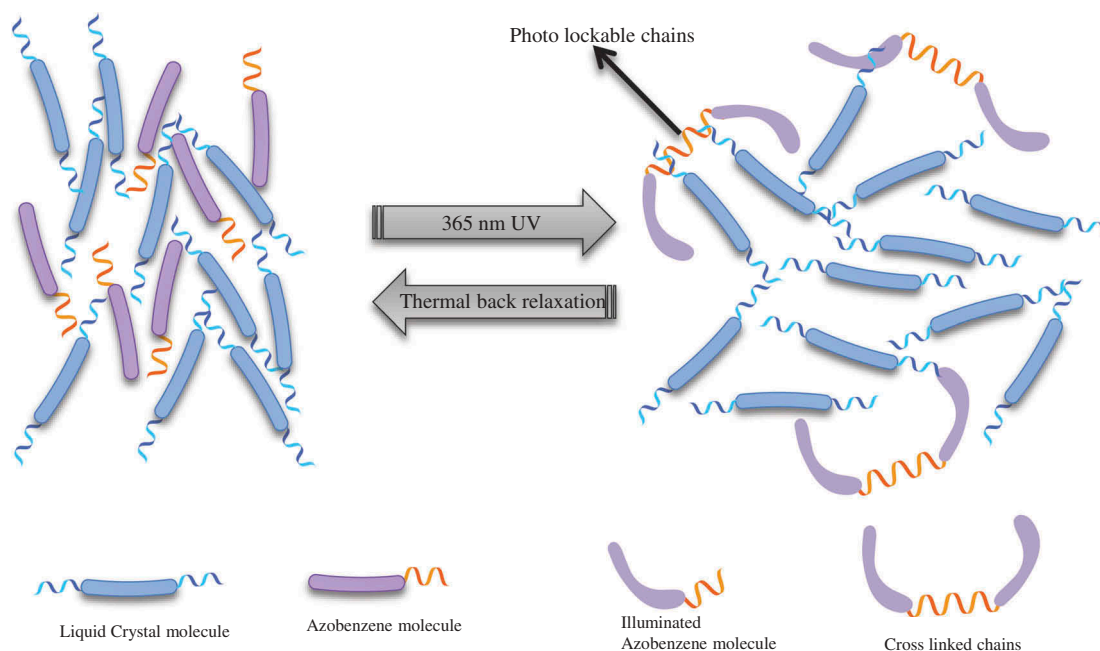
All the compounds, ethyl 4-amino benzoate (Fluka), sodium nitrite (Fluka), phenol (Merck), Hydrochloric acid (Merk), 5-Bromo 1-pentene (Fluka), sodium hydroxide (Fluka), potassium iodide (Fluka), potassium carbonate (Aldrich), 4-Fluoro phenol (Fluka), 4-Chloro phenol (Fluka), 4-Bromo phenol (Fluka), 4-Iodo phenol (Fluka), 1,3-dicyclohexylcarbodiimide (DCC) (Fluka), 4-(*N,N*-dimethylamino)pyridine (DMAP) (Fluka),

##### Analytical data of the dyes.

##### (1): Ethyl 4-(4-hydroxyphenylazo) benzoate (3).

Ethyl 4-aminobenzoate (**1**) (46.00 mmol, 1 equiv.) dissolved in methanol (40 ml), cooled the solution to 2°





**Figure 6.** (colour online) Model explaining the mechanism of photolocking when guest-host effects were employed. One can see that due to the formation of intermolecular locking chains; system takes longer time to reverse back to their original shape

C. Hydrochloric acid (25%) added drop-wise (8.7 ml) to the reaction mixture maintaining sub-zero temperature.  $\text{NaNO}_2$  dissolved with water (44.6 mmol, 1 equiv.) added drop-wise at  $2^\circ\text{C}$  and the reaction mixture stirred for 15 min to produce diazonium ion (2). Finally, the phenol solution in methanol (44.6 mmol, 1 equiv.) added slowly at  $2^\circ\text{C}$ , further basified using 0.1 N NaOH to pH 8.5–9 and the reaction mixture agitated for 4 h.

Diluted the above reaction mixture with cold methanol (250 ml) and acidified to pH 4. The reddish yellow precipitate filtered, dried and recrystallised from methanol.

Reddish-yellow coloured solid;  $R_f = 0.42$  (40%  $\text{CH}_2\text{Cl}_2$ -EtOH); yield: 62%; m.p.:  $160$ – $161^\circ\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$ : 3321, 3186, 1728, 1602, 1484, 1248, 1140, 829;  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ):  $\delta$  8.17 (d,  $J = 8.2$  Hz, 2 H, Ar), 7.92 (d,  $J = 7.5$  Hz, 2 H, Ar), 7.88 (d,  $J = 7.5$  Hz, 2 H, Ar), 7.01 (d,  $J = 8.2$  Hz, 2 H, Ar), 5.54 (s, 1 H, OH),  $\delta$  4.42 (q,  $J = 7.2$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 1.44 (t, 3 H,  $\text{CH}_2\text{CH}_3$ ).

**(2): Ethyl 4-{(E)-[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate (4)**

Ethyl 4-(4-hydroxyphenylazo) benzoate (3) (18.5 mmol, 1 equiv.), 5-Bromo 1-pentene (37.1 mmol, 2 equiv.) dissolved in dry acetone (300 ml) and potassium carbonate (18.5 mmol, 1 equiv.) added in portion, also a pinch of potassium iodide added to reaction mixture. The above reaction mixture refluxed for 24 h under nitrogen atmosphere and confirmed the product formation by TLC, further

the solvent removed under reduced pressure using rotavapour, dried the reaction mixture and taken for the next ester hydrolysis reaction.

**(3): 4-{(E)-[4-(Pent-4-en-1-yloxy)phenyl]diazenyl}benzoic acid (5)**

Ethyl 4-{(E)-[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate (4) dissolved in 100 ml of methanol and cooled below  $5^\circ\text{C}$ , a aqueous solution of potassium hydroxide (62.2 mmol, 3 equiv.) in water (20 ml) added drop wise, refluxed for 4 h. Further TLC confirmed the completion of reaction, followed by *n*-hexanes washes to remove nonpolar impurities. Further, acidified the aqueous solution with dilute hydrochloric acid to pH 6 and then extracted with ethyl acetate, followed by brine solution wash. Organic ethyl acetate layer dried over anhydrous sodium sulphate and filtered, further the filtrate evaporated under reduced pressure using rotavapour to obtain solid followed by recrystallisation using ethanol: chloroform (2:1) to accomplish pure acid.

A yellow coloured solid; yield: 46%; m.p.:  $156$ – $157^\circ\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$ : 2849, 2918, 3004, 1711, 2918, 1220, 1588, 1493, 1248, 1130, 1092, 835;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.10 (s, 1H, OH), 7.13–8.12 (m,  $J = 8.15$  Hz, 8H, Ar), 5.93–5.83 (m, 1H, olefinic), 5.10 – 4.99 (m, 2H, olefinic), 4.12 (t,  $J = 8.00$  Hz, 2H,  $\text{OCH}_2$ ), 2.42 – 2.59 (m, 4H,  $\text{CH}_2$ ).

**(4): Phenyl/4-halogen-phenyl4-{(E)-[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate derivative (6-H to 6-I)**

4- $\{(E)-[4-(\text{Pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoic acid (**5**) (15.3 mmol, 1 equiv.) dissolved in 50 ml of dry dichloromethane, DMAP (1.40 mmol, 0.1 equiv.) added and the mixture stirred for 30 min. A solution of either phenol or 4-halogen-phenol (15.2 mmol, 1 equiv.) in dry dichloromethane (10 ml) added to the mixture. *N,N'*-dicyclohexylcarbodiimide (DCC) (23.0 mmol, 1.5 equiv.) in 10 ml of dry dichloromethane added slowly and stirred the reaction mixture for 24 h at room temperature. The precipitate *N,N'*-dicyclohexylurea filtered off and the filtrate was concentrated, followed by column chromatography (230–400 silica gel) using  $\text{CHCl}_3:\text{CH}_3\text{OH}$  (9:0.5) as an eluent and further purified by crystallisation from  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (2:1) to afford pale yellow colour solid.

**6-H:** Phenyl 4- $\{(E)-[4-(\text{pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoate; pale yellow coloured solid; yield: 64%; m.p.: 119–121°C; IR (KBr)  $\text{cm}^{-1}$ : 3004, 2918, 2849, 1732, 1200, 1143, 1261, 1096, 1072, 859, 838;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (d, 2H,  $J = 8$  Hz, Ar), 8.03 (d, 2H,  $J = 8$  Hz, Ar), 7.98 (d, 2H,  $J = 8$  Hz, Ar), 7.92 (d,  $J = 8$  Hz, 2H, Ar), 7.65 (d,  $J = 8$  Hz, 1H, Ar), 7.52 (d,  $J = 8$  Hz, 2H, Ar), 7.18 (d,  $J = 8$  Hz, 2H, Ar), 5.89 (m, 1H,  $-\text{CH}=\text{CH}_2$ , olefinic), 5.10 (m, 2H,  $-\text{CH}=\text{CH}_2$ , olefinic), 4.13 (m, 2H,  $\text{OCH}_2$ ), 2.23–1.89 (m, 2H,  $2 \times \text{CH}_2$ ); EA calc. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_3$ , 386.44 g/mol: calculated (found) %: C 74.59 (74.50), H 5.74 (5.67), N 7.25 (7.13).

**6-F:** 4-Fluoro-phenyl 4- $\{(E)-[4-(\text{pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoate; pale yellow coloured solid; yield: 63%; m.p.: 126–127°C; IR (KBr)  $\text{cm}^{-1}$ : 3006, 2916, 2848, 1725, 1186, 1143, 1261, 1096, 1072, 858, 838;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32 (d, 2H,  $J = 8$  Hz, Ar), 8.02 (d, 2H,  $J = 8$  Hz, Ar), 7.97 (d, 2H,  $J = 8$  Hz, Ar), 7.58 (d,  $J = 8$  Hz, 2H, Ar), 7.39 (d,  $J = 8$  Hz, 2H, Ar), 7.18 (d,  $J = 8$  Hz, 2H, Ar), 5.90 (m, 1H,  $-\text{CH}=\text{CH}_2$ , olefinic), 5.09 (m, 2H,  $-\text{CH}=\text{CH}_2$ , olefinic), 4.14 (m, 2H,  $\text{OCH}_2$ ), 2.24–1.88 (m, 2H,  $2 \times \text{CH}_2$ ); EA calc. for  $\text{C}_{24}\text{H}_{21}\text{FN}_2\text{O}_3$ , 404.43 g/mol: calculated (found) %: C 71.27 (71.23), H 5.23 (5.19), N 6.93 (6.89).

**6-Cl:** 4-Chloro-phenyl 4- $\{(E)-[4-(\text{pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoate; pale yellow coloured solid; yield: 65%; m.p.: 131–132°C; IR (KBr)  $\text{cm}^{-1}$ : 3006, 2916, 2851, 1733, 1259, 1208, 1143, 1092, 1066, 837, 809;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.35 (d, 2H,  $J = 8$  Hz, Ar), 8.01 (d, 2H,  $J = 8$  Hz, Ar), 7.96 (d, 2H,  $J = 8$  Hz, Ar), 7.57 (d, 2H,  $J = 8$  Hz, Ar), 7.41 (d, 2H,  $J = 8$  Hz, Ar), 7.18 (d,  $J = 8$  Hz, 2H, Ar), 5.88 (m, 1H,  $-\text{CH}=\text{CH}_2$ , olefinic), 5.10 (m, 2H,  $-\text{CH}=\text{CH}_2$ , olefinic), 4.12 (m, 2H,  $\text{OCH}_2$ ), 2.22–1.86 (m, 2H,  $2 \times \text{CH}_2$ );  $^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  164.38, 162.72, 155.59, 149.86, 149.65, 138.35, 131.77, 130.75, 130.40, 130.00, 125.69, 124.40, 123, 115.84,

115.71, 67.75, 30.01, 29.55, 29.49, 29.30; EA calc. for  $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{O}_3$ , 420.89 g/mol: calculated (found) %: C 68.49 (68.78), H 5.03 (5.29), N 6.66 (6.44).

**6-Br:** 4-Bromo-phenyl 4- $\{(E)-[4-(\text{pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoate; pale yellow coloured solid; yield: 63%; m.p.: 142–143°C; IR (KBr)  $\text{cm}^{-1}$ : 3016, 2919, 2848, 1733, 1259, 1208, 1143, 1092, 1066, 837, 809;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32 (d, 2H,  $J = 8$  Hz, Ar), 8.02 (d, 2H,  $J = 8$  Hz, Ar), 7.98 (d, 2H,  $J = 8$  Hz, Ar), 7.85 (d, 2H,  $J = 8$  Hz, Ar), 7.39 (d, 2H,  $J = 8$  Hz, Ar), 7.17 (d,  $J = 8$  Hz, 2H, Ar), 5.90 (m, 1H,  $-\text{CH}=\text{CH}_2$ , olefinic), 5.07 (m, 2H,  $-\text{CH}=\text{CH}_2$ , olefinic), 4.12 (t,  $J = 8.1$  Hz, 2H,  $\text{OCH}_2$ ), 2.24–1.84 (m, 2H,  $2 \times \text{CH}_2$ ); EA calc. for  $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{O}_3$ , 465.34 g/mol: calculated (found) %: C 61.95 (62.01), H 4.55 (4.29), N 6.02 (6.14).

**6-I:** 4-Iodo-phenyl 4- $\{(E)-[4-(\text{pent-4-en-1-yloxy})\text{phenyl}]\text{diazanyl}\}$ benzoate; pale yellow coloured solid; yield: 64%; m.p.: 158–159°C; IR (KBr)  $\text{cm}^{-1}$ : 3033, 2916, 2848, 1731, 1257, 1205, 1139, 1068, 1052, 859, 836;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (d, 2H,  $J = 8$  Hz, Ar), 8.01 (d, 2H,  $J = 8$  Hz, Ar), 7.98 (d, 2H,  $J = 8$  Hz, Ar), 7.70 (d, 2H,  $J = 8$  Hz, Ar), 7.35 (d, 2H,  $J = 8$  Hz, Ar), 7.18 (d,  $J = 8$  Hz, 2H, Ar), 5.88 (m, 1H,  $-\text{CH}=\text{CH}_2$ , olefinic), 5.10 (m, 2H,  $-\text{CH}=\text{CH}_2$ , olefinic), 4.12 (t,  $J = 8$  Hz, 2H,  $\text{OCH}_2$ ), 2.22–1.85 (m, 2H,  $2 \times \text{CH}_2$ ); EA calc. for  $\text{C}_{24}\text{H}_{21}\text{IN}_2\text{O}_3$ , 512.34 g/mol: calculated (found) %: C 56.26 (55.96), H 4.13 (4.28), N 5.47 (5.19).

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