# THE EFFECT OF SUBSTITUENTS ON THERMAL AND OPTICAL PROPERTIES OF AZOBENZENE-CHOLESTERYL DERIVATIVES

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## ABSTRACT

Structurally isomeric cholesteryl-appended azobenzene derivatives with various substituents, such as H/unsubstituted, ether and ester, at the terminal position of azobenzene units were designed, synthesized and characterized spectroscopically. The effect of substituents on the thermal and optical properties of all the derivatives were studied. The results from thermogravimetric analysis (TGA) revealed that all the derivatives were stable up to 283 °C and start to degrade thereafter. In addition, the ether derivatives exhibited lower thermal stability than the other derivatives. It is likely that the presence of ether linkage at the terminal position introduced greater flexibility to the azobenzene and, consequently, reduced thermal stability. The ether and ester derivatives underwent two-stage decomposition when heated up to 600 °C; the first stage between 320-350 °C due to the breaking of ether and ester linkages, and the second stage between 440-490 °C due to the breaking of carbonate linker which connect azobenzene to the cholesteryl unit. However, the unsubstituted (H-substituted) derivative underwent only one-stage degradation at 386 °C due to the cleavage of the carbonate linker. Results from the differential scanning calorimetry (DSC) revealed that the melting transition temperature ( $T_m$ ) of the ester derivatives exhibited *trans-cis* isomerization when irradiated with UV light. The rate of photolysis of ether was faster (2 min) than both ester and the unsubstituted derivatives (5 min). These results revealed that substituents at the terminal position of azobenzene are able to influence thermal and optical properties under given conditions.

Keywords: Azobenzene, Cholesteryl derivatives, Thermal properties, Optical properties, Photoisomerization.

# 1. INTRODUCTION

Azobenzene is aromatic molecule, derived by replacing the hydrogen atom of diazene (-NH = NH-) by phenyl ring. Azobenzene exist in two different forms: a thermally stable *trans* configuration and meta-stable *cis*-configuration. During the photolysis, the trans form isomerized in to *cis* form and *cis*-to-*trans* is observed under visible light or under heat (thermally). This transformation of *trans*-to-*cis* and vice versa is completely reversible process. In addition to that, it is observed that the trans isomer is more stable (50–100 kJ/mol) than the *cis* isomer (200 kJ/mol) (Mita *et al.* 1989; Monti *et al.* 1982; Schulze *et al.* 1977). Due to photo tunable isomerization properties, azobenzene have received much attention in research areas both fundamental and applied sciences.

The effect of substitution on the benzene ring of the azobenzene causes strong electronic absorption band between UV to near IR (NIR) region, which facilitate the fine-tuning of the

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color chemically. The absorption band of the azobenzenes can be tuned by introducing substituent at the aromatic ring. For example, substitution of electron donating group or push/pull substituent at the para position of the benzene ring leads to shifting of absorption to longer wavelength (Mahimwalla *et al.* 2012). Any substitution on the ring leads to change the spectroscopic properties as well as the isomerization mechanism. By varying the substituents, long wavelength switching, photo-bleaching stability and stability to hydrolysis can be fabricated into a photo-switch. Photosensitivity of the azobenzenes can be increased to visible electromaganetic radiation and extending their potential application by expanding the absorption wavelengths of the azobenzene towards redshift (bathochromic effect) (Conti *et al.* 2008; Delaire and Nakatani 2000; Yesodha *et al.* 2004).

The absorption spectrum of *trans*-azobenzene exhibit two well separated band in the UV visible region. One is strong band at 320 nm, due to  $\pi$ - $\pi$ \* transition and other band one is weak band at 450 nm in the visible region due to n- $\pi$ \* transition. However, in the case of *cis*-azobenzene n- $\pi$ \* absorbs more strongly than *trans*-azobenzene, but  $\pi$ - $\pi$ \* transitions are weaker. *Trans*-*cis* isomerization follows the S1  $\leftarrow$  S0 and S2  $\leftarrow$  S0 excitation whereas the *cis*-trans isomerization takes place by exciting in to S1 or S2 state (Bortolus and Monti 1979; Hamon *et al.* 2009; Qin *et al.* 2015).

Due to high stability of *cis* form and the reversibility of the isomerization, azobenzene and its derivatives are attracted in the designing of photo switchable materials(Merino and Ribagorda 2012), photonic bandgap materials (Zhang *et al.* 2012) and micro/nanoscale device applications (Muraoka *et al.* 2006; Sun *et al.* 2012; Yamada *et al.* 2008). Therefore, there are wide variety of azobenzene derivatives raised by changing the geometry by introducing different electron withdrawing/donating substituents bonded to the aromatic moieties (Iqbal and Samiullah 2013).

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Cholesteryl group is rigid and planar molecule with a steroidal skeleton of four fused ring system (Albuquerque et al. 2018). In recent years, the research on cholesteryl-based compounds have increased attention due to an attractive starting material, as a model system for organic synthesis, easy functionalization and low cost. Especially, cholesteryl based liquid crystals and gelators have attracted much attention because of their range of applications including alternative biomaterials (Yusa et al. 1998; Zhou et al. 2009) for drug delivery or tissue engineering (Draper and Adams, 2017; Skilling et al. 2014), liquid crystalline displays(Tan et al. 2016), photochemical molecular switches etc. Therefore, it was expected that by combining both azobenzene and cholesteryl units, one could tune the thermal and optical properties. Based on that combination few reports can be found in the literature, in which it was used to tune the sol-gel (gelator) and liquid crystalline phase transitions (Geng et al. 2017; Jiao et al. 2012; Liu et al. 2011; Tan et al. 2016; Yang et al. 2012). The neat azobenzene (without any flexible chain) do not possess liquid crystalline behavior. However incorporation of cholesteryl unit into the azobenzene, the resulting derivatives exhibit variety of mesogenic behavior. Therefore, in this report, we designed azobenzene-cholesteryl derivatives with different substituents at the terminal position of the azobenzene unit in order to make it useful for photonics application. This manuscript mainly focusing on the effect of substituent on the thermal and optical properties the designed molecules.

#### 2. MATERIALS AND METHODS

#### 2.1 Materials

All chemicals were purchased from Aldrich Chemicals and used without further purification. All solvents were purified before use. Aniline, *p*-anisidine, ethyl-4-aminobenzoate, (–)-cholesteryl chloroformate, and 4-(dimethylamino) pyridine were purchased from Sigma-Aldrich and used without further purification. Triethylamine and N,N'-dicyclohexyl-carbodiimide (Aldrich) were used as received. Dichloromethane was distilled over calcium hydride under argon immediately before use and all solvents were purified and dried by standard procedures before use.

#### 2.2 Instrumentation

Fourier transform infrared spectra (FTIR) were recorded using a Fourier transform infrared (FTIR) spectrophotometer (Spectrum One, PerkinElmer). Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-500 (Darmstadt, Germany) high-resolution NMR spectrometer, and the chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. Differential scanning calorimetry (DSC) was conducted using a PerkinElmer DSC-7 at heating and cooling rates of 10 °C min<sup>-</sup> under a nitrogen atmosphere. TGA thermograms were recorded using the TA instruments TGA-2050 thermal analysis system. Photoisomerization behavior was investigated by observing absorption between 320 and 420 nm on a Jasco V-770 spectrophotometer. A UV-Visible spectrophotometer was used to record the spectra in a chloroform solution  $(10^{-5}M)$ . The typical procedure adopted was as follows: At various time intervals, the solution was exposed to UV irradiation from a 125 W medium pressure mercury lamp kept at a distance of 10 cm from the sample. After this, UV absorption was measured on the spectrophotometer. This procedure was repeated until the reduction of absorption was completed.

## 2.3 Synthesis of compounds Ia-Ic

Compounds Ia-Ic were synthesized according to the reported procedures (Nickmans et al. 2018). For example, compound 1c, namely ethyl-4-[(4-hydroxyphenyl)diazenyl]benzoate, was synthesized as follows: Typically, about 9.03g (1.0 equiv., 55.0 mmol) of ethyl-4-amino-benzoate was placed in a round-bottom flask and dissolved in 1M HCl. This solution was stirred at 0 °C. An aqueous solution of 3.80 g (1.0 equiv., 55.0 mmol) of sodium nitrite in 25 mL of water was added dropwise to this solution to produce a diazonium salt solution. Meanwhile, 9.61 g (1.65 equiv., 90.8 mmol) of sodium carbonate and 5.81 g (1.0 equiv., 55.0 mmol) of phenol were dissolved in 100 mL of water at 0 °C. The diazonium salt solution was then added dropwise to this solution and stirred for 3 h at 0 °C. Then, the condenser of the flask was neutralized with 1M hydrochloric acid to precipitate the product. The precipitate that formed was then filtered off, air-dried, and recrystallized in ethanol to obtain a pure compound as an orange solid (yield of 74%). Using the same procedure, the other azo compounds, namely compounds Ia and Ib, were synthesized; however, aniline (for Ia) and *p*-anisidine (for Ib) were used instead of ethyl-4-amino-benzoate.

FT-IR (KBr,  $v_{max}/cm^{-1}$ ) : 3463 (-OH), 1517, 1580 (C-C in Ar), 1728 (C = O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500MHz,  $\delta$  in ppm) : 8.4 (d, 2H, Ar-C-COO), 8.19 (d, 2H, Ar-H), 7.9–8.0 (m, 4H, Ar-C-N), 7.0 (d, 2H, Ar-C-OH), 5.79 (broad, s, -OH), 4.38 (q, 2H, O-CH<sub>2</sub>), 1.39 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>).

#### 2.4 Synthesis of compound IIa

Compound IIa was synthesized as follows: Compound 1a (1.98 g, 10 mmol) and triethylamine (3.036 g, 30 mmol) were placed in a double neck round bottom flask with nitrogen inlets and dissolved in dry chloroform. Next, a small amount of 4-(dimethylamino)pyridine (DMAP) dissolved in chloroform was slowly added to this solution and stirred constantly under a nitrogen atmosphere. Then, cholesteryl chloroformate (4.491 g, 10 mmol) dissolved in chloroform was added dropwise to the solution through a funnel. After this addition, the reaction mixture was stirred at room temperature for 48 h. Next, the contents of the flask were extracted with excess chloroform and washed with aqueous sodium bicarbonate, a brine solution, and water. This procedure was used to obtain the organic phase, which was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was recrystallized from ethanol to obtain a pure final compound (yield 79%).

FT-IR (KBr,  $v_{max}/cm^{-1}$ ) : 2868, 2947 (CH<sub>2</sub>), 1764 (C = O), 1500, 1586 (C-C in Ar), 1247 (COC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500MHz,  $\delta$  in ppm) : 7.97–7.90 (m, 4H), 7.53–7.47 (d, 2H), 7.36–7.34 (m, 2H), 7.26 (t, 1H), 5.44 (d, 1H), 4.66 (m, 1H), 2.51–1.33 (m, 28H), 1.09 (s, 3H), 0.93 (d, 3H), 0.87 (d,6H), 0.69 (s, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  152.91, 150.21, 139.05, 131.07, 129.07, 124.05, 123.28, 121.65, 79.13, 77.25, 56.66, 56.12, 49.97, 42.30, 39.69, 39.50, 37.92, 36.82, 36.54, 36.17, 35.78, 31.90, 31.83, 28.21, 28.00, 27.63, 24.27, 23.82, 22.81, 22.55, 21.04, 19.27, 18.71, 11.85.

A similar procedure was adopted for the synthesis of precursors IIb and IIc, using Ib and Ic instead of Ia as in the above procedure.

Compound IIb: Yield: 73%; FT-IR (KBr,  $v_{max}/cm^{-1}$ ) : 2869, 2942 (CH<sub>2</sub>), 1762 (C = O), 1503, 1593 (C-C in Ar), 1247 (COC). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.92–7.89 (m, 4H), 7.33–7.26 (d, 2H), 7.02–7.00 (m, 2H), 5.43 (d, 1H), 4.69 (m, 1H), 3.88 (s, 3H), 2.51–1.33 (m, 28H), 1.08 (s, 3H), 0.93 (d, 3H), 0.87 (d, 6H), 0.68 (s, 3H).  ${}^{13}$ C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  162.11, 152.58, 150.34, 146.88, 139.06, 124.76, 123.69, 121.56, 114.19, 79.05, 77.25, 56.65, 56.11, 55.54, 49.95, 42.29, 39.68, 39.50, 37.91, 36.81, 36.53, 36.16, 35.17, 31.88, 31.82, 28.20, 27.99, 27.62, 24.26, 23.82, 22.80, 22.55, 21.03, 19.26, 18.70, 11.84

Compound IIc: Yield: 76%; FT-IR (KBr,  $v_{max}/cm^{-1}$ ) : 2867, 2949 (CH<sub>2</sub>), 1763 (C = O), 1718 (C = O), 1497, 1602 (C-C in Ar), 1255 (COC). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.20–8.19 (d, 2H), 8.18 (d, 2H), 7.99–7.92 (m, 4H), 7.37–7.36 (m, 2H), 7.26 (t, 1H), 5.43 (d, 1H), 4.43–4.39 (m, 1H), 2.50–1.33 (m, 28H), 1.17 (s, 3H), 0.99 (d, 3H), 0.87 (d, 6H), 0.68 (s, 3H). 13C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  165.99, 154.92, 153.48, 150.10, 139.01, 132.24, 130.55, 124.38, 123.30, 122.60, 121.74, 79.21, 77.25, 61.25, 56.65, 56.12, 49.96, 42.29, 39.68, 39.49, 37.90, 36.81, 36.53, 36.16, 35.77, 31.89, 28.20, 27.99, 27.61, 24.26, 23.81, 22.80, 22.54, 21.03, 19.26, 18.70, 11.84.

### 3. RESULTS AND DISCUSSION

#### 3.1 Synthesis and Characterization

The synthetic route for the preparation of azobenzene and cholesteryl-based conjugates (IIa-c) are shown in Scheme 1. The photosensitive azobenzene derivatives (Ia-c) were obtained through the reaction of sodium phenoxide with the respective *p*-substituted aniline in the presence of nitrous acid (diazonium salt). All the azo derivatives were purified by repeated recrystallization in hot ethanol. The azo derivatives (Ia-c) obtained were then further reacted with cholesteryl chloroformate in the presence of triethylamine in chloroform or dichloromethane and that reaction produced compounds IIa-c with the yield of 73-79%. All the compounds were purified by recrystallization in ethanol and found to be soluble in DMF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and acetone; and found to be insoluble in ethanol, methanol, and toluene. The structures of the IIa-c compounds were confirmed by FT-IR, <sup>1</sup>H and <sup>13</sup>C-NMR analysis. All the spectral values were in accordance with the assigned structures.

The FT-IR spectra of compounds IIa-c are shown in Fig. 1 and reveal strong absorption bands at > 1760 cm<sup>-1</sup> corresponding to the carbonyl group (C = O) of the carbonates which link the azobenzene with the cholesteryl units. This indicated that the formation of IIa-c from Ia-c was successful. Compound IIc showed one more carbonyl stretching at 1718 cm<sup>-1</sup> which revealed the presence of ester (-COOC<sub>2</sub>H<sub>5</sub>) at the terminal position.

The <sup>1</sup>H-NMR spectra of compounds IIa-c are shown in Fig. 2. The presence of aromatic protons between 7-8 ppm and the presence of alkene protons (C = CH) at 5.43 ppm confirmed the presence of azobenzene and cholesteryl units in the structure. All other alkane protons in the cholesteryl units resonated between 0.5 and 2.0 ppm. The <sup>13</sup>C-NMR values for all the compounds are depicted in Fig. 3. The presence of peaks at approximately 150 ppm and 121 ppm corresponding to carbonyl (C = O in carbonates) and -C = CH- carbon (in the cholesteryl unit) confirmed the successful formation of compounds IIa-c. All the spectral values were in accordance with the structure of the molecule.



Fig. 1 FTIR spectra of compound IIa-c



Scheme 1 Synthesis of azobenzene-cholesteryl derivatives





#### 3.2 Thermal Properties

The thermal behavior of the azobenzene-cholesteryl derivatives (IIa-c) was evaluated by TGA under a nitrogen atmosphere at a heating rate of 10 oC/min; the traces of all the derivatives are shown in Figure 4 and the data are illustrated in Table 1. The thermal stability of all the derivatives was evaluated by 5 and 50% weight loss at minimum temperature. The results showed that the derivatives were stable up to 283 oC and then started degrading thereafter under a nitrogen atmosphere. The thermal stability of the derivatives revealed the following order: IIb < IIa < IIc. These results showed that the thermal stability of IIb was lower than that of IIa which indicated that the unsubstituted azo derivative possessed higher thermal stability than when ether was substituted. It is likely that the presence of ether linkage at the terminal position introduced greater flexibility to the azobenzene and, consequently, reduced the thermal stability to lower than that of the unsubstituted, which had a more rigid structure.

From Figure 4, it can be seen that compound IIa underwent only one-stage degradation at 386 °C, whereas compounds IIb and IIc underwent two-stage degradation. The first stage of degradation for compound IIb was at 321 °C, whereas for compound IIc it was at 349 °C. This may have been due to the cleavage of ether and ester linkages in IIb and IIc, respectively (Balamurugan and Kannan 2008). Since esters are stronger than ether linkages, IIc underwent a greater amount of degradation than IIb. Similarly, the second stage of degradation of IIb and IIc was at 444 °C and 489 °C, respectively. This second stage of degradation arose due to the breaking of the carbonate linkage [O-C(=O)-O-] between azobenzene and the cholesteryl units. Compound IIa underwent only one-stage degradation which corresponded to the breaking of the carbonate linkage. These results indicated that the incorporation of substituents at the terminal position greatly affected the thermal stability of the compounds studied. The char yields of all the compounds were measured at 600 °C and the data ascribed that the compound IIb possessed a higher char yield than the rest of the compounds, suggesting that compound IIb possessed better flame-retardant properties than the others. This may have been due to the electron activating nature of the methoxy group (Mohan Kumar et al. 2007). The increasing order of the char yields were as follows: IIa < IIc < IIb.

In addition to TGA, all the compounds were subjected to DSC analysis. Figure 5 shows the DSC thermograms during the heating cycle from room temperature (30 °C) to 250 °C. From this figure, it can be observed that the compounds IIa-c exhibited only one endothermic peak at 181 °C, 177 °C and 186 °C, respectively. These endothermic peaks were likely due to the melting phase transition of the compounds under the given conditions. The lower value for IIb could be attributed to the introduction of a methoxy substituent (ether) which increased the flexibility of the molecule, thereby reducing the rigidity and affecting the melting phase transition of the molecule more so than for the unsubstituted (IIa) and ester substituted (IIc). These results, once again, demonstrated the effect of an ether substituent at the terminal position on flexibility.

| The first decomposition (dides of compounds fig | Table 1 | Thermal | decompo | osition | values o | f Com | pounds | Ha- |
|---|---------|---------|---------|---------|----------|-------|--------|-----|
|---|---------|---------|---------|---------|----------|-------|--------|-----|

| Compound | TGA             |                  |                        |  |  |
|----------|-----------------|------------------|------------------------|--|--|
| Compound | <sup>a</sup> 5% | <sup>b</sup> 50% | % of Residue at 600 °C |  |  |
| IIa      | 307             | 348              | 0.90                   |  |  |
| IIb      | 295             | 326              | 16.02                  |  |  |
| IIc      | 316             | 360              | 10.81                  |  |  |

<sup>a</sup> Temperature corresponding to 5 wt % loss.

<sup>b</sup> Temperature corresponding to 50 wt % loss.



Fig. 4 The TGA thermograms of compounds IIa-c



Fig. 5 The DSC thermograms of compounds IIa-c

#### 3.3 Optical properties

The effects of photoirradiation of all the compounds were studied by irradiating them under UV-vis light and recording the changes. The photolysis of the compounds IIa-c in chloroform under UV irradiation are shown in Figures 6a-c. As expected for typical azobenzene, the absorption maximum values of IIa-c were 323, 347 and 329 nm, respectively, and as the  $\pi$ - $\pi$ \* transition band of the *trans*-isomers decreased, new absorbance maximum values appeared at 435, 443 and 439 nm due to the n- $\pi$ \* transition band of the *cis*-isomers (Balamurugan *et al.* 2014).

From this figure, it is interesting to note that photolysis took place at a much faster rate and that the absorption band at 323– 347 nm completely disappeared within 3-5 min of irradiation. In addition, compound IIb underwent rapid photolysis and was saturated within 2 min of irradiation compared to the other compounds, which took 3-5 min. This may have been due to the presence of the ether (methoxy substituent) linking group at the terminal position of the azobenzene. The rate of photolysis was in the following order:

IIb > IIa > IIc.

This order corresponded to the thermal properties of the compounds. These results suggest that the presence of a substituent at the terminal position of the azobenzene unit played a vital role in altering the thermal and optical properties of the compounds studied. Reversibility of the cis-trans form occurred when treated with visible light.



Fig. 6 Changes in UV spectral characteristics during photolysis of IIa-c solutions in chloroform (10  $\mu$ M)

# 4. CONCLUSION

Cholesteryl-appended azobenzene derivatives with various terminal substituents were synthesized. The thermal and optical properties of all the derivatives were studied with regard to the various substituents at the terminal position of the azobenzene unit. The results revealed that the introduction of an ether (methoxy) substituent lowered the thermal stability and increased the rate of photolysis (*trans-cis* isomerization); whereas the reverse trend was observed for the ester derivative. The thermal and optical properties of the unsubstituted derivative were found to lie between the ether and ester derivatives. These results provide valuable information on the tuning of thermal and optical properties through the introduction of substituents at the terminal position of azobenzene-cholesteryl derivatives. The application of the above-synthesized derivatives towards the development of tunable photonic band gap materials are under progress.

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# **COMPETING INTERESTS**

The authors declare no competing interests.

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