Synthesis and Characterization of Monomers

2.1 Introduction

Aromatic diols containing bis (azo) and o-nitrobenzyl chromophores were synthesized and characterized. The monomers with tailor-made photoresponsive properties viz, Bis (4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane and Bis (4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane were synthesized on the basis of reported procedures. These compounds were characterized by $^{13}$C NMR, $^1$H NMR, IR and UV-Vis spectroscopy and elemental analysis. Other monomers viz, Isophorone diisocyanate (IPDI), 2, 4-Toluene diisocyanate (2, 4-TDI) and Hexamethylene diisocyanate (HMDI) and the catalyst dibutyltin dilaurate (DBTDL) were used as received.

2.2 Experimental

2.2.1 Materials and Methods

IR spectra were recorded on IFS 66U FTIR spectrometer. $^1$H NMR spectra were recorded on JEOL model GSX 400 MHz spectrometer and $^{13}$C NMR spectra were obtained using Bruker 300 MHz spectrometer with TMS as internal standard. UV-Vis-spectra were obtained using Schimadzu UV-2100 spectrophotometer. The chromophores were purified by column chromatography using 100-200 mesh silica gel and appropriate mixture of benzene and ethylacetate-benzene mixture for elution. The solvents were distilled before use for column chromatography. The purity of the crude and recrystallised products was
monitored both by UV and TLC measurements. TLC was performed on glass plate coated with silica gel GF254 containing 13% calcium sulphate as binder. Appropriate solvents were used for development and the developed plates were visualized by exposure to iodine. Spectroscopic grade solvents were used for all measurements.

2.2.2 Synthesis and characterization of 4, 4'-Diamino-2, 2'-dinitrodiphenylmethane (2b)

4, 4'-diaminodiphenylmethane (m.p 92 °C) [2a] was nitrated\(^2\) using a mixture of anhydrous potassium nitrate and 98% sulphuric acid at 0 °C. A solution of potassium nitrate (0.05 mol, 5.05 g) in conc. sulphuric acid (18 M, 40 mL) at 0 °C was added to an ice-cold solution (0-5 °C) of 4, 4'-diaminodiphenylmethane (0.025 mol, 5 g) in conc. sulphuric acid (18 M, 40 mL) dropwise during a period of half an hour, with stirring. The stirring was continued for another 3 h, keeping the reaction mixture at 0 °C. The reaction mixture was diluted by pouring it over crushed ice and was then neutralized with ice-cold 1:1 ammonia solution. The orange-yellow precipitate was collected on a filter, washed thoroughly with water and dried. This product was recrystallised from ethylalcohol-ethyl acetate mixture (90:10). Orange-red flakes of 4, 4'-diamino-2, 2'-dinitrodiphenylmethane were obtained (m.p.204-206 °C).

Yield: 5.1 g (70.2%)

IR (KBr, cm\(^{-1}\)): 1329, 1520 [N-O stretch of C-NO\(_2\)]; 3447, 3366 [-NH\(_2\)].

\(^1\)H NMR (CDCl\(_3\), δ): 3.0 [2H (s), Ph-CH\(_2\)-Ph, b]; 4.8 [4H (s), amino protons, a];

7.8 [2H (d), aromatic, e]; 7.4 [2H (d), aromatic, d]; 8 [2H (s), aromatic, e].

\(^13\)C NMR (CDCl\(_3\)): 32 [methylenes, (7)], 124 (2), 130 (4), 135 (6), 157 (5),

159 (1), 170 (3) [aromatic].
2.2.3 Synthesis and characterization of Bis (4-hydroxyphenylazo)-2, 2'-
dinitrodiphenylmethane (2c)

To an ice-cold solution of 4, 4'-diamino-2, 2'-dinitrodiphenylmethane (6.25 mmol, 1.8 g) in sulphuric acid (6 M, 15 mL), was added aqueous sodium nitrite solution (1.1 g, 5 mL) in drops over a period of 10 minutes, with stirring. The excess of nitrous acid formed was destroyed with 0.75 g of solid urea. The diazonium salt solution was diluted with ice-cold water and the pH of the solution was maintained at 7-7.5 by adding solid sodium acetate. It was added dropwise to a cold alkaline solution of phenol (12.5 mmol, 0.8 mL). The reaction mixture was cooled and kept for 2h. The brown solid was collected, washed well
with water, petroleum ether and dried. It was recrystallised from ethylalcohol- ethyl acetate mixture (m.p 372 °C).

Yield: 1.92 g (62%)

IR (KBr, cm⁻¹): 1274 [C-O stretch of Ph-OH]; 1531, 1350 [N-O stretch of C-NO₂]; 1603 [-N=N-, trans]; 2925, 2856 [-CH₂ stretch]; 3421 [-OH stretch].

UV (λ_max, 2-propanol, nm): 248 [-NO₂]; 364 [-N=N-]

¹H NMR (CD₃COCD₃, δ): 3.2 [2H (s), Ph-CH₂-Ph, b]; 9.10 [2H (s), OH, a];

7.8-8 [8H (m), aromatic, c and d]; 8.77-8.1 [6H (m), aromatic, e-g].

¹³C NMR (CDCl₃, δ): 32 [methylene, (11)], 116 (2), 120 (4), 127 (3), 135 (6), 137 (10), 139 (8), 144 (5), 153 (9), 155 (1), 170 (7) [aromatic].

CHN analysis: Calculated for (C₂₅H₁₈N₆O₆): C-60.24; H-3.61; N-16.86

Found: C-60.20; H-3.58; N-16.78.

Fig. 2.3. ¹H NMR assignments of 2c

Fig. 2.4. ¹³C NMR assignments of 2c
2.2.4 Synthesis and characterization of 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2, 2'-dinitrodiphenylmethane (2d)

4, 4'-diamino-2, 2'-dinitrodiphenylmethane was diazotized and coupled with 1:1 mixture of phenol and o-cresol using the procedure adopted for synthesizing 2c. To an ice-cold solution of 2b (0.025 mol, 7.2 g) in sulphuric acid (6 M, 50 mL), was added an aqueous solution of sodium nitrite (4.4 g, 20 mL) over a period of 20 minutes with stirring. The excess of nitrous acid formed was destroyed with 3 g of solid urea. The diazotized solution was coupled with an alkaline solution of a mixture of phenol (0.025 mol, 1.6 mL) and o-cresol (0.025 mol, 2.6 mL), by maintaining the pH of the solution at 7-7.5. The brown solid was collected, washed with water, petroleum ether, dried and the isomer was isolated by column chromatography using ethylalcohol-ethyl acetate mixture (m.p. 368°C).

Yield: 7.7 g (60%).

IR (KBr, cm⁻¹): 1274 [C-O stretch of Ph-OH]; 1352, 1530 [N-O stretch of C-NO₂]; 1594 [- N=N-]; 2924, 2853 [-CH₂ stretch]; 3412 [OH-stretch].

UV (λmax, 2-propanol, nm): 250 [-NO₂ ]; 382 [-N=N-]

¹H NMR (CD₃COCD₃, δ): 2.29 [3H (s), CH₃, k]; 3.25 [2H (s), Ph-CH₂-Ph, b]; 9.12 [1H (s), OH, a1]; 9.2 [1H (s), OH, a2]; 7.77 -7.72 [3H (m), aromatic, e-e]; 8-7.8 [4H (m), aromatic, f and g]; 8.77 -8.1 [6H (m), aromatic, h-j].

¹³C NMR (CDCl₃, δ): 20 [methyl, (12)]; 32 [methylene, (11)]; 117 (2 and 18), 120 (16), 121 (4), 123 (14), 126 (17), 128 (3), 132 (15), 135 (6), 138 (8), 146 (5), 148 (10), 153 (9), 156 (1), 157 (13), 170 (7) [aromatic].
2.2.5 Synthesis and characterization of Bis (4-hydroxy-3-methylphenylazo)-2, 2'-dinitrodiphenylmethane (2e)

The diazonium chloride prepared by reacting an ice-cold solution of 2b (0.0218 mol, 6.3g) in sulphuric acid (6 M, 45 mL) with aqueous sodium nitrite solution (4.4 g, 70 mL) was coupled with an alkaline solution of o-cresol (0.044 mol, 4.55 mL) at 0-5 °C and the pH of the solution was maintained at 7-7.5 by adding solid sodium acetate before the
addition of o-cresol. The brown solid was collected, washed with water, ether, dried and recrystallized from ethylalcohol-ethyl acetate mixture (m.p. 365 °C).

Yield: 6.65g (58%).

IR (KBr, cm⁻¹): 1275 [C-O stretch of Ph-OH]; 1349, 1530 [N-O stretch of C-NO₂]; 1595 [-N=N-]; 2928, 2852 [-CH₂ stretch]; 3411 [-OH stretch].

UV (λmax, 2-propanol, nm): 255.5 [-NO₂]; 385.5 [-N=N-].

^1^H NMR (CD₃COCD₃, δ): 2.29 [6H (s), two CH₃, i]; 3.3 [2H (s), Ph-CH₂-Ph, b]; 9.2 [2H (s), OH, a]; 7.77 -7.72 [6H (m), aromatic, c-e]; 8.77 -8.1 [6H (m), aromatic, f-h].

^1^C NMR (CDCl₃): 20 [methyl, (7)], 32 [methylene, (14)], 116 (6), 120 (4), 124 (2), 128 (5), 131 (3), 135 (9), 137 (11), 139 (13), 146 (8), 154 (12), 157 (1), 170 (10) [aromatic].

CHN analysis: Calculated for (C₂₇H₂₂N₆O₆): C-61.6; H-4.18; N-15.97.

Found: C-61.12; H-4.15; N-15.94

![Fig. 2.7. ^1^H NMR assignments of 2e](image)

![Fig. 2.8. ^1^C NMR assignments of 2e](image)
2.3 Results and discussion

The reaction involved a diazo coupling between a diazotized aromatic amine viz, 4, 4'-diamino- 2, 2'-dinitrodiphenylmethane (2b) and a coupling component, phenol / o-cresol (scheme 2.1). This electrophilic substitution reaction is regioselective and leads to a high yield of the para isomer. For the dinitro derivative 2b, the IR peaks at 1520 and 1329 cm⁻¹ confirmed the nitro substitution. In the $^{13}$C NMR spectrum of 2b, there were only six peaks due to aromatic carbons. This indicated that the nitro groups were substituted in a symmetrical fashion in both the phenyl rings. This was further confirmed by $^1$H NMR signals at δ 7.4 to 8.

In the case of the dihydroxy compounds, 2c / 2d / 2e, the IR peaks due to – OH groups were observed at 3421 / 3412 / 3411 cm⁻¹ respectively and their C – O stretch were observed at ~1274 cm⁻¹. The peak between 1594 and 1603 cm⁻¹ was due to the azo group. In the UV-Vis spectra, the peaks observed at 364 / 382 / 385 nm were due to the azo group ($\pi \rightarrow \pi^*$) and the peaks at 248 / 250 / 255 nm were due to the nitro groups. In $^{13}$C NMR spectra of 2c / 2d / 2e, ten, fifteen and twelve signals were observed respectively, due to aromatic carbons, the signal due to methylene carbon was observed at 32 ppm and the signal due to methyl carbon was observed at 20 ppm. The elemental analysis of 2c, 2d and 2e also confirmed the proposed structures (scheme 2.1). This was further confirmed by the $^1$H NMR spectra. In this spectra, the peaks due to phenolic protons were observed at δ 9.10 / 9.12; 9.2 / 9. 2, the peaks due to methylene protons were observed at δ 3.2 / 3.25 / 3.3 respectively, the peaks due to aromatic protons were observed between δ 7.8 - 8, 8.77 - 8.1 and 7.77 - 7.72 and the peak due to methyl protons were at δ 2.29.
2.4 Conclusion

The bis (4-hydroxyphenylazo)-2, 2'-dinitrodiphenylmethane and its derivatives could be used as the monomers for the synthesis of a wide variety of novel co-polymers such as polyesters, polyamides and polyurethanes which may be used as starting materials for the study of the photochemistry of nitro groups as well as azo groups in a constrained environment.
2.5 References
