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SYNTHESIS AND CHARACTERIZATION OF INTERMEDIATE AZOBENZENE DERIVATIVES WITH TERMINAL POLAR GROUPS

BY

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Abstract. The paper presents synthesis and characterization of some intermediate azobenzene compounds containing polar ending groups with the purpose to obtain final bent-core liquid crystals with potential semiconducting properties. The azobenzene compounds were synthesized by diazotization and condensation reaction of the corresponding amine derivatives, 4-(trifluoromethyl)aniline and 4-aminobenzonitrile followed by esterification with 3-hydroxybenzoic acid protected previously with benzyl chloride. All the synthesized compounds were purified by recrystallization or column chromatography and their structures were confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ studies.

Keywords: azoderivatives; 3-hydroxybenzoic acid; 4-(trifluoromethyl)aniline; 4-aminobenzonitrile.

1. Introduction

Liquid crystals (LCs) are among the most successful of the electronic materials yet developed for consumer product applications. In addition to being

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widely appreciated by the public and commonly used in every-day life, the study of LC materials in the context of display applications now constitutes a mature academic field. Molecular structure and shape are essential parameters to form liquid crystalline phases. Various structures can be created by the particular chemical design of the mesogenic molecules. Although the molecular shape contributes to the formation of the phase structure, determines its physical properties as well. Certain structural features are often found in molecules forming liquid crystalline phases. The existence of strong dipoles and easily polarizable groups in the molecule seems important. The withdrawing or donating electronic groups may strongly affect the electronic density, the molecular flexibility and the partial polarity of the molecule. An electron withdrawing group, such as F, Cl, CN, NO₂, NCS or OCF₃ can pull electron density away from a π -conjugated system either through a resonance or inductive effect (Khan *et al.*, 2018; Pal *et al.*, 2017). Substitution on a conjugated core with electron withdrawing groups generally leads to enhanced stability toward oxidation and a change in molecular packing while in the case of liquid crystals influence the temperature transition as well.

Bent-core molecules containing azo linkages present remarkable properties because of the association of the photosensitive nature of azobenzene derivatives with ferroelectric liquid crystalline properties of bent-core compounds. During the isomerization, the physical and chemical properties of these photochromic compounds can also be changed, including refractive indices, dielectric constants, geometrical structures, energy levels, polarity, magnetic properties and oxidation/reduction potentials. These controllable property tunings have inspired people to apply photochromic system in photoelectric field such as photo-switches, sensors, molecular machine, data storage, liquid crystal, and so on (Fleischmann and Zentel, 2013).

Our efforts have been focussed on lowering the transition temperatures so that they are better suited for easy physical characterization. Thus, unsymmetric bent-shaped nematogens with low transition temperatures and wide nematic mesophase domains were designed and synthesized (Scutaru *et al.*, 2018; Simion *et al.*, 2016; Simion *et al.*, 2015; Huzum *et al.*, 2013).

Thus, in the present study we purposed to synthesize new intermediate compounds with polar cyano or trifluoromethane substituents at one end of azobenzene unit that will be used further to obtain bent-core final compounds.

The intermediate azobenzene derivatives I and II were synthesized in a convergent manner. First, 3-hydroxybenzoic acid was protected with benzyl chloride, followed by esterification with azophenolic compounds substituted with highly polar groups -CN and -CF₃. The azophenolic compounds were synthesized by diazotization of 4-(trifluoromethyl)aniline or 4-aminobenzonitrile and the resulted diazonium salts were coupled to phenol (Fig. 1).

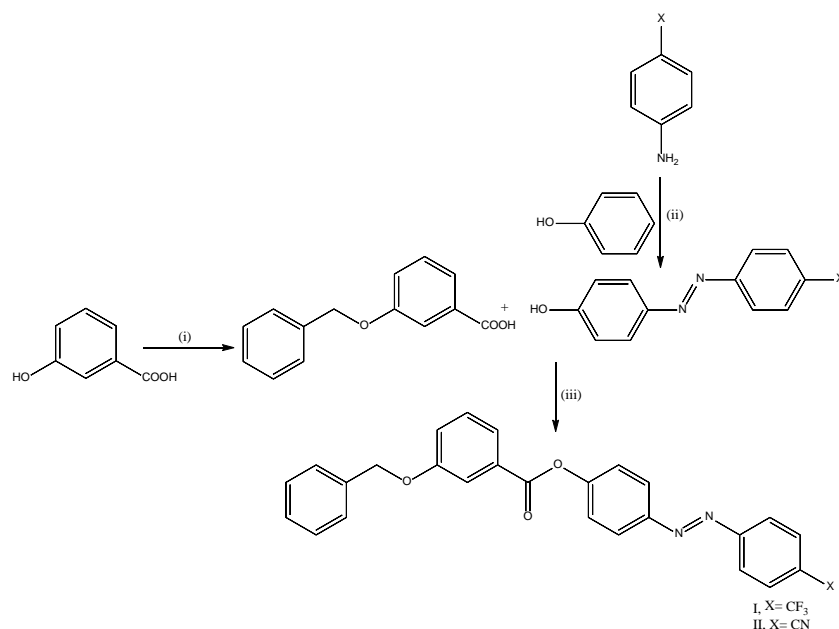


Fig. 1 – Synthetic route followed to obtain the intermediate compounds: (i) benzyl chloride, K₂CO₃, KI; (ii) NaNO₂, phenol; (iii) DCC, DMAP, CH₂Cl₂.

All the synthesized compounds were purified by recrystallization and column chromatography and the structures were confirmed by NMR studies.

2. Experimental

2.1. Reagents and Chemicals

The starting materials such as 3-hydroxybenzoic acid, 4-(trifluoromethyl)aniline, 4-aminobenzonitrile, benzyl chloride were obtained from (Aldrich) and were used without further purification. The synthesized compounds were purified by column chromatography with Silica gel 60 (Merck). All organic solvents (acetone, dichloromethane, ethyl acetate, hexanes) used in chemical synthesis and for purification the reaction products were purchased from Chemical Company (Romania) were dried, distilled (conventional methods) or used as bought.

2.2. NMR Characterization

NMR spectra were recorded in CDCl₃ at 298 K on a Bruker Avance DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard.

2.3. Synthesis

3-(benzyloxy)benzoic acid

To 0.13 mole (10 g) 3-hydroxybenzoic acid dissolved in 100 mL acetone 0.3 mole (30 g) K_2CO_3 and catalytic amount of KI were added. After refluxing 30 minutes, 8.282 mL benzyl chloride were added and refluxed for another 24 hours. The formed precipitate was washed with acetone and the filtrate was evaporated. The crude product was purified by the column chromatography. Over yellow oily resulted compound, 50 mL hot ethanol and 0.03 mole (1.2 g) NaOH dissolved in 15 mL water were added and the mixture was refluxed for 4 hours. After cooling, the solution was treated with HCl until pH = 2 and the resulted precipitate was filtered off and washed with water. The product was purified by CC/silicagel/dicloromethane:ethyl acetate = 20:1. Yield: 64% (2.194 g), white crystals, mp = 139°C. 1H NMR (400 MHz, $CDCl_3$) δ /ppm: 7.27 (m, 2H, Ar); 7.48 (m, 6H, Ar); 7.27 (m, 1H, Ar); 5.15 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ /ppm: 172.29, 159.08, 136.75, 130.88, 129.91, 128.97, 128.46, 127.88, 123.26, 121.54, 115.80, 70.51.

4-Hydroxy-4'-trifluoromethyl-azobenzene

To 1.296 g (8.04 mmol) 4-(trifluoromethyl)aniline dissolved in a solution of 2.68 mL concentrated HCl and 0.804 mL CH_3COOH , 0.55 g (8.04 mmol) $NaNO_2$ in 0.8 mL H_2O were added dropwise at temperature below 5°C. The obtained diazonium salt was added further to 0.801 g (8.52 mmol) phenol dissolved in a solution containing 0.3 g NaOH, 5.01 g Na_2CO_3 in 28.8 mL H_2O . After 2 hours of stirring at room temperature, the precipitated product was filtered off and washed with water. The residue was purified by crystallisation from hexane. Yield: 40% (2.14 g), orange crystals, mp = 130°C 1H NMR (400 MHz, $CDCl_3$) δ /ppm: 7.98 (m, 4H, Ar); 7.77 (d, 2H, Ar); 7.01 (d, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$) δ /ppm: 160.00, 154.35, 146.97, 132.20, 131.88, 126.61, 126.21, 122.98, 116.46.

4-Hydroxy-4'-cyanoazobenzene

To 16 g (26.8 mmol) 4-amino-benzonitrile dissolved in 13.62 mL H_2SO_4 50%, 1.8 g (26.8 mmol) $NaNO_2$ in 9 mL H_2O were added dropwise at temperature below 5°C. The obtained diazonium salt was added further to 2.56 g (27.2 mmol) phenol dissolved in 30 mL NaOH 2N. After 2 hours of stirring at room temperature, the precipitated product was filtered off and washed with water. The residue was purified by crystallisation from hexane. Yield: 80% (4.78 g), orange crystals, mp = 203°C. 1H NMR (400 MHz, DMSO) δ /ppm: 10.05, (s, 1H), 8.01 (d, 2H, Ar); 7.92 (d, 2H, Ar); 7.86 (d, 2H, Ar), 6.98 (d, 2H, Ar). ^{13}C NMR (400 MHz, DMSO) δ /ppm: 161.89, 154.08, 145.04, 133.48, 125.43, 122.55, 118.35, 115.94, 111.99.

General synthesis of compounds I and II

To phenol dissolved in dichloromethane with 3 drops of THF, 3-(benzyloxy)benzoic acid dissolved dichloromethane and catalytic amount of DMAP were added. After 30 minutes of stirring, DCCI dissolved in dichloromethane was added and the reaction mixture was stirred for 3 hours at room temperature. The formed precipitate was washed with dichloromethane and the filtrate was evaporated. The crude product was purified by the column chromatography.

4-((4-cyanophenyl)diazenyl)phenyl 3-(benzyloxy)benzoate (I)

Quantities: 4-hydroxy-4'-cyanoazobenzene (22 mmol, 0.503 g), 3-(benzyloxy)benzoic acid (20 mmol, 0.482 g), DCCI (22 mmol, 0.455 g). Purification CC/silicagel/dichloromethane:hexane = 20:1. Yield: 98% (0.897 g), orange crystals, mp = 156°C. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 8.07 (d, 2H, Ar); 8.02 (d, 2H, Ar); 7.87 (m, 4H, Ar); 7.5 (m, 3H, Ar); 7.44 (m, 4H, Ar); 7.39 (d, 1H, Ar); 7.31 (m, 1H, Ar), 5.17 (s, 2H). ¹³C NMR (400 MHz, CDCl₃) δ/ppm: 164.49, 158.83, 154.30, 153.82, 149.91, 136.28, 133.17, 130.29, 129.74, 128.63, 128.15, 127.51, 124.63, 123.32, 122.84, 122.54, 121.04, 118.40, 115.73, 113.94, 70.20.

4-((4-(trifluoromethyl)phenyl)diazenyl)phenyl 3-(benzyloxy)benzoate (II)

Quantities: 4-hydroxy-4'-trifluoromethyl-azobenzene (3.63 mmol, 0.967 g), 3-(benzyloxy)benzoic acid (3.30 mmol, 0.753 g), DCCI (3.96 mmol, 0.818 g). Purification CC/silicagel/dichloromethane:hexane = 20:1. Yield: 94 % (1.491 g), orange crystals, mp = 175°C. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 8.08 (m, 4H, Ar); 7.87 (m, 4H, Ar); 7.50 (m, 7H, Ar); 7.39 (m, 1H, Ar); 7.31 (m, 1H, Ar); 5.18 (s, 2H). ¹³C NMR (400 MHz, CDCl₃) δ/ppm: 164.59, 158.90, 154.31, 153.57, 150.05, 136.36, 132.41, 132.09, 130.43, 129.76, 128.66, 128.19, 127.55, 126.31, 124.50, 123.03, 122.89, 122.50, 121.08, 115.76, 70.27.

3. Conclusions

Two intermediate azobenzene compounds were synthesized by condensation of azophenolic derivatives with protected 3-hydroxybenzoic acid. The structure of the compounds were confirmed by ¹H-NMR and ¹³C-NMR studies. The intermediate compounds will be used further to synthesize final bent-core derivatives with potential semiconducting liquid crystalline properties.

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SINTEZA ȘI CARACTERIZAREA UNOR COMPUȘI AZOBENZENICI INTERMEDIARI CU GRUPĂRI TERMINALE POLARE

(Rezumat)

Articolul prezintă sinteza și caracterizarea unor compuși azobenzenici intermediari conținând grupări terminale polare, în scopul obținerii ulterioare de cristale lichide de tip bent-core cu potențiale proprietăți semiconductoare. Compușii azobenzenici au fost sintetizați prin reacții de diazotare și cuplare ale aminelor corespunzătoare, 4-trifluorometil anilină și 4-amino benzonitril, urmate de esterificarea cu acidul 3-hidroxibenzoic protejat la gruparea fenolică cu clorură de benzil. Toți compușii au fost purificați prin recristalizare sau prin cromatografie pe coloană, iar structurile lor au fost confirmate prin studii $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.