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## SYNTHESIS AND CHARACTERIZATION OF AZOBENZENE ALKYLATED MESOGEN WITH FLUORINE SUBSTITUENT

BY

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**Abstract.** The paper presents synthesis and characterization of azobenzene compound that contains 10 carbon atoms as flexible terminal chain and one fluorine atom as lateral polar substituent. The synthesis was achieved by diazotization of 4-amino benzoic acid and coupling of diazonium salt to 2-fluorophenole, followed by alkylation with a bromoalkyl compound. The synthesized compounds were purified and their structures were confirmed by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  studies.

**Keywords:** diazotization, coupling, fluorine, alkylation.

### 1. Introduction

One of the most effective electronic materials synthesized to date are liquid crystals (LCs). Compared to the liquid and solid states, liquid crystals have different molecular configurations and constitute a separate state of matter (Andrienko, 2006). Liquid crystals have electronic and optical functions that make them suitable for a wide range of engineering applications, including displays, sensors, electro-photonics and so forth (Bisoyi and Li, 2016; Sunil *et*

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*al.*, 2020). Materials that exhibit liquid crystalline phases are called mesogens. The physical properties of mesogens are influenced by the molecular shape so that the designing of a liquid crystalline compound with particular technical applications represent a challenge for chemists, physicists and engineers. Generally, the structure of a calamitic liquid crystal consists in a planar structure induced by aromatic cycles connected by different linking groups which ensures both the rigidity of the system and the orientational order of the molecular axes (Mo *et al.*, 2021). The most frequent linking group that connect two aromatic cycle into mesogenic unit is azo linkage. When exposed to UV and visible light, compounds with azo groups in their molecules undergo isomerization changes. The intramolecular interactions of the mesogens are impacted by reversible trans-cis photoisomerization and modifications to the size, shape and polarity of the azobenzene group, which results in a disorder of the macroscopic structure (Goodby *et al.*, 2012; Alaasar, 2016; Wang *et al.*, 2020). The calamitic mesogenic structure must contain as well a flexible unit that provide flexibility and mobility and prevent the crystallization. The presence of strong polar groups close to molecule's core increase the mesomorphism of the molecule (Han *et al.*, 2016). Due to the large electronegativity of the fluorine atom, the presence of such substituent on calamitic mesogens reduce the electron density at the carbon of a C-F bond while unshared electron pairs of fluorine bonded to a  $sp^2$  carbon resonate with  $\pi$ -electrons and increases the electron density at the ortho-(or para-) carbon of aromatic compounds (Hiyama, 2015). Considering the electron-withdrawing effect of the fluorine substituent, organic acids become much more acidic by fluorine substitution.

In the present paper we report the synthesis and characterisation of azobenzene compound alkylated with 10 carbon atoms and substituted with one fluorine atom.

## 2. Experimental

### 2.1. Reagents and chemicals

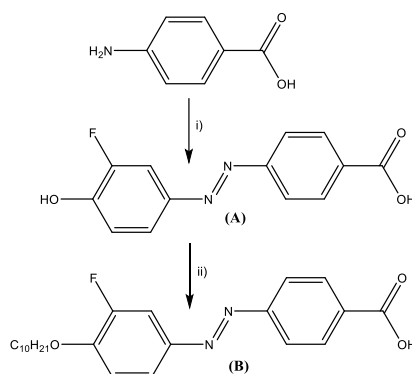
For the synthesis of compounds, 4-aminobenzoic acid (>97%), 2-fluorophenol (98%), 1-bromodecane obtained from (Sigma-Aldrich) were used without further purification. The synthesized compounds were purified by column chromatography with Silica gel 60 or  $Al_2O_3$  (Merck, Darmstadt, Germany). All organic solvents (acetone, dichloromethane, diethyl ether, ethyl acetate, hexanes) used in the chemical synthesis or purification were purchased from Chemical Company (Iași, Romania) were dried, distilled or used as bought.

## 2.2. NMR Characterization

Confirmation of the structures of the compounds was obtained by NMR spectra that were recorded in deuterated solvents on a Bruker Avance DRX 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS) as internal standard.

## 2.3. Synthesis

The synthesis was accomplished by diazotizing 4-amino benzoic acid and coupling of resulted diazonium salt to 2-fluorophenol. The resulted azo compound (A) was alkylated further with 1-bromodecane, leading to compound (B) (Scheme 1).



Scheme 1 – Schematic route for the preparation of azobenzene derivative: (i) HCl, NaNO<sub>2</sub>, 2-fluorophenol, CH<sub>3</sub>COONa · 3H<sub>2</sub>O, (ii) C<sub>10</sub>H<sub>21</sub>Br, KOH, KI, EtOH, reflux.

### *Synthesis of 4-((3-fluoro-4-hydroxyphenyl)diazenyl)benzoic acid (A)*

Over a mixture of 1 g (7.30 mmol) 4-aminobenzoic acid and HCl (2.09 mL), 0.50 g (7.23 mmol) NaNO<sub>2</sub> 20% aqueous solution was added dropwise. During this addition, the temperature was kept in 0 - 5°C temperature domain. After the addition of nitrite, the diazonium salt was left on the ice bath for 30 minutes, then was added dropwise over a solution of 0.84 g (7.52 mmol) 2-fluorophenol in 9.93 g (73 mmol) sodium acetate trihydrate solution (15 mL H<sub>2</sub>O). The resulting suspension was left to stir for 60 minutes, then filtered and thoroughly washed with water. The yellow crystals were purified by Soxhlet using ethyl acetate.  $\eta$  = 56% (1.06 g), yellow solid, m.p. = 275°C. <sup>1</sup>H-NMR (DMSO, 400MHz)  $\delta$ : 13.15 (br.s, 1H, -OH), 10.99 (s, 1H), 8.11 (d, 2H, Ar-H, J= 8.5), 7.89 (d, 2H, Ar-H, J= 8.5 Hz), 7.72 (m, 2H, Ar-H, ), 7.17 (t, 1H, Ar-H, J=8.8 Hz). <sup>13</sup>C-NMR (DMSO, 100MHz)  $\delta$ : 166.78, 154.27, 152.66, 149.44, 149.31, 144.97, 132.432, 130.63, 122.33, 117.67, 108.34.

*Synthesis of 4-((4-(decyloxyphenyl)-3-fluorophenyl)diazenyl)benzoic acid (B)*

In a 50 mL round-bottomed flask 0.8 g (3.076 mmol) 4-((3-fluoro-4-hydroxyphenyl)diazenyl)benzoic acid dissolved in 10 mL absolute ethanol was placed followed by the addition of 0.46 g (8.21 mmol) KOH dissolved in 2 mL of absolute ethanol and 0.5 mL H<sub>2</sub>O, a catalytic amount of KI and 0.747 g (3.383 mmol) 1-bromodecane. The reaction mixture was refluxed under stirring for 15 hours. The solvent was evaporated and the solid residue was dissolved in water. The solution was washed with diethyl ether for three times and then was made strongly acidic with HCl 32%.  $\eta = 40\%$  (0.494 g), orange solid. <sup>1</sup>H-NMR (DMSO, 400MHz)  $\delta$ : 8.13 (d, 2H, Ar-H, J= 8.5), 7.91 (d, 2H, Ar-H, J= 8.5 Hz), 7.83 (d, 1H, Ar-H, J= 8.8 Hz), 7.71 (dd, 1H, Ar-H, J<sub>1</sub>=12.1 Hz, J<sub>2</sub>=2.1 Hz), 7.38 (t, 1H, Ar-H, J=8.8 Hz), 4.19 (t, 2H, -O-CH<sub>2</sub>-), 1.78 (m, 2H, -CH<sub>2</sub>-), 1.44 (m, 2H, -CH<sub>2</sub>-), 1.33 (m, 12H, -CH<sub>2</sub>-), 0.86 (t, 3H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO, 100MHz)  $\delta$ : 166.27, 154.03, 150.66, 149.75, 145.54, 132.41, 130.18, 122.68, 121.95, 114.53, 107.30, 69.86, 30.89, 28.54, 28.50, 28.26, 28.24, 28.14, 24.95, 21.64, 13.44.

### 3. Conclusions

An azobenzene monofluorurated derivative was synthesized and characterized by two steps, consisting in diazotization/coupling and alkylation reactions. The obtained compound will be further used in synthesis of materials with potential liquid crystalline properties.

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#### SINTEZA ȘI CARACTERIZAREA UNUI MEZOGEN AZOBENZENIC ALCHILAT CU UN ATOM DE FLUOR CA SUBSTITUENT

(Rezumat)

Articolul redă sinteza și caracterizarea unui compus azobenzenic care conține 10 atomi de carbon drept catenă flexibilă terminală și un atom de fluor ca substituent lateral polar. Sinteza s-a realizat prin diazotarea acidului 4-amino benzoic și cuplarea sării de diazoniu la 2-fluorofenol, urmată de alchilarea cu un compus bromoalchilic. Compușii sintetizați au fost purificați iar structurile lor au fost confirmate de datele  $^1\text{H-NMR}$  și  $^{13}\text{C-NMR}$ .