Synthetic, Mesomorphic, and DFT Investigations of New Nematogenic Polar Naphthyl Benzoate Ester Derivatives

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Abstract: Four new non-symmetrical derivatives based on central naphthalene moiety, 4-((4–(alkoxy) phenyl) diazenyl)naphthalen–1–yl 4–substitutedbenzoate (I_n/x), were prepared, and their properties were investigated experimentally and theoretically. The synthesized materials bear two wing groups: an alkoxy chain of differing proportionate length (n = 6 and 16 carbons) and one terminal attached to a polar group, X. Their molecular structures were elucidated via elemental analyses and FT-IR and NMR spectroscopy. Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were carried out to evaluate their mesomorphic properties. The results of the experimental investigations revealed that all the synthesized analogues possess only an enantiotropic nematic (N) mesophase with a high thermal stability and broad range. Density functional theory (DFT) calculations were in accordance with the experimental investigations and revealed that all prepared materials are to be linear and planar. Moreover, the rigidity of the molecule increased when an extra fused ring was inserted into the center of the structural shape, so its thermal and geometrical parameters were affected. Energy gap predictions confirmed that the I_{16c} derivative is more reactive than other compounds.

Keywords: fused ring; azo/ester; mesomorphic properties; liquid crystals materials; optimized structures; DFT; thermal parameters

1. Introduction

Calamitic liquid crystals (LCs) are widely used in LC displays and optical systems because of the suitability of their anisotropic properties [1–3]. However, their thermal and optical properties, though, can be adjusted by modifying the molecular geometries of the mesogenic compounds. Therefore, to develop a new LC material, the correlation between the geometry of its mesogenic part and its mesomorphic properties should be understood. Several calamitic azo/ester LC derivatives have been investigated and evaluated based on their optical properties [4,5]. From these geometrical investigations, one can determine the ester orientation within the rigid portion, the location of azo/ester linkages, lateral groups, and the terminal flexible–chain length [6–13]. A rigid shape creates azobenzene molecules, which are essential for exhibiting mesomorphic phenomena [14,15]. Moreover, their properties may lead to molecular mobility in terms of response to light or heat, thus offering many opportunities for photonic application [16–21].

It was found that the insertion of a lateral group on the aromatic ring of the mesogenic part influenced the mesophase transition temperature range of the smectic phases [22–24].
and increased spontaneous polarization [25]. The existence of mesophases near room temperature is very important for potential applications; consequently, lateral moieties are incorporated into the molecular architecture to lower the melting temperature [26]. On the other hand, polar terminal substituents and linking moieties were both important factors for the designed compounds, in terms of the formation, kind, thermal stability, and range of the observed mesophase [5,12,27–40].

Simulations of computational calculations for the molecular-shaped parameters offered interesting correlations between the experimental findings and theoretical predictions [41–52].

Recently, many homologous series have been documented based on naphthalene-core LCs [53–57]. In our previous study [45], a homologous series of (E)-4-(4-(hexyloxyphenyl diazenyl)naphthalene-1-yl-4′-alkoxybenzoate was synthesized and its mesomorphic properties evaluated. The recently documented series were found to exhibit an enantiotropic nematic (N) mesophase. Moreover, our research lab has focused its attention on the computational investigations of newly, synthesized liquid crystalline materials to correlate their mesomorphic behavior with the theoretical calculations. The geometrical structure of LCs plays an essential role on the thermal stability and formation of their mesophases. Additionally, it has been found that the addition of extra fused ring in the mesogenic portion of the molecule results a new geometrical property and nematic mesophase predominant observed [45]. Further, the length of alkoxy terminal chains has essential role in the formation, stability, kind, and mesomorphic range of LC derivatives. In this investigation, we extended our studies to evaluate the effect of additional terminal polar substituents having a different polarities and sizes. The aim was to synthesize new derivatives based on a central naphthalene group (I_{n/x}) bearing two terminals (the alkoxy proportion group and a terminal attached to a polar substituent (X), Scheme 1) to investigate their mesomorphic properties via experimental and theoretical approaches.

![Scheme 1](image)

Scheme 1. The synthetic compounds, I_{n/x}.

2. Experiment

Synthesis

The liquid crystalline compounds I_{n/x} were synthesized according to the following Scheme 2.
Figure 1. $^1$H NMR of 4-((4-(hexyloxy)phenyl)diazenyl)naphthalen-1-yl 4-methoxybenzoate, I$_{6/a}$ as a prototype.
4-((4-(hexadecyloxy)phenyl)diazenyl)naphthalen-1-yl 4-methoxybenzoate, \( I_{16/a} \)

Yield: 91.2%; mp 87.0 °C, FTIR (\( \tilde{\nu} \), cm\(^{-1}\)): 2935, 2845 (CH\(_2\) stretching), 1725 (C=O), 1590 (N=N), 1162 (C–O\(_{\text{ester}}\)), 1080 (C–O\(_{\text{alkoxy}}\)). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)SO) \( \delta \) 8.95–8.92 (m, 1H, Naph–H), 8.23 (d, \( J = 8.9 \) Hz, 2H, Naph–H), 8.00 (d, \( J = 9.0 \) Hz, 2H, Naph–H), 7.90 (m, 1H, Ar–H), 7.82 (d, \( J = 8.2 \) Hz, 1H, Ar–H), 7.75 (m, 1H, Ar–H), 7.69–7.65 (m, 1H, Ar–H), 7.57 (d, \( J = 6.6 \) Hz, 1H, Ar–H), 7.19–7.13 (m, 4H, Ar–H), 4.10 (t, \( J = 7.7 \) Hz, 2H, 3.85 (s, 3H), 1.77–1.65 (m, 6H), 1.60–1.54 (m, 4H), 1.49–1.33 (m, 4H), 1.26–1.15 (m, 6H), 1.11–0.94 (m, 8H), 0.77–0.67 (m, 3H). Elemental Analysis calc. (found): C, 74.02 (74.06); H, 5.78 (5.75); Cl, 5.78 (5.75).

4-((4-(hexadecyloxy)phenyl)diazenyl)naphthalen-1-yl 4-fluorobenzoate, \( I_{16/c} \)

Yield: 93.0%; mp 114.0 °C, FTIR (\( \tilde{\nu} \), cm\(^{-1}\)): 2944, 2848 (CH\(_2\) stretching), 1726 (C=O), 1595 (N = N), 1162 (C–O\(_{\text{ester}}\)), 1080 (C–O\(_{\text{alkoxy}}\)). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)SO) \( \delta \) 8.90 (m, 1H, Naph–H), 8.23 (m, 2H, Naph–H), 8.00 (m, 2H, Naph–H), 7.90 (m, 1H, Ar–H), 7.85 (d, \( J = 8.1 \) Hz, 1H, Ar–H), 7.78(m, 1H, Ar–H), 7.68–7.63 (m, 1H, Ar–H), 7.57 (m, 1H, Ar–H), 7.18–7.10 (m, 4H, Ar–H), 4.12 (t, 2H), 1.77–1.53 (m, 6H), 1.49–1.32 (m, 4H), 1.29–1.17 (m, 4H), 1.09–0.97 (m, 8H), 0.91 (m, 6H), 0.74 (m, 3H). Elemental Analysis calc. (found): C, 74.68 (74.66); H, 7.55 (7.54); Cl, 5.65 (5.63); N, 4.47 (4.45).

3. Results and Discussion

3.1. Mesomorphic and Optical Behaviour

The mesomorphic and optical characteristics of the present azo/ester derivatives, \( I_{n/x} \) were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Figure 2 shows an example of the DSC thermograms of 4-((4-(alkoxy)phenyl)diazenyl)naphthalen-1-yl 4-methoxybenzoate (\( I_{16/a} \)) for the heating and cooling cycles. The N–mesophase schlieren textures observed under POM for the analogues \( I_{16/c} \) are shown in Figure 3. The mesophase transition temperatures and their associated enthalpies were determined by DSC and are presented in Table 1. All designed derivatives, bearing the central naphthyl moiety, exhibited two transition heating and cooling peaks on DSC thermogram scans. These were ascribed to a Cr-to-N mesophase and associated enthalpies were determined by DSC and are presented in Table 1. All designed derivatives, bearing the central naphthyl moiety, exhibited two transition heating and cooling peaks on DSC thermogram scans. These were ascribed to a Cr-to-N mesophase and associated enthalpies were determined by DSC and are presented in Table 1.
system that has terminal alkoxy chains of proportionate length, affected the mesophase transition phenomena, which depended on the location and mesomeric function of the selected substituent (i.e., donating (CH$_3$O) or withdrawing (F and Cl moieties). Furthermore, the introduction of terminals into an LC material will have two opposing effects: first, it will decrease the phase stability due to the steric effect of the terminal substituent [59–63]; secondly, the molecular anisotropy will increase or decrease depending on the polarizing effect of the substituent. The dipole moment of the whole compound depends mainly on the position and polarity of the attached lateral and terminal groups. In addition, the terminal and lateral moieties played an essential role in the observed melting temperatures of the synthesized derivatives. Table 1 and Figure 4 show the decrease in the nematic range and stability of the laterally substituted derivatives in the following order: $I_{6/a} > I_{16/c} > I_{6/b} > I_{16/a}$.

![DSC thermogram](image)

**Figure 2.** The second heating and cooling scan of a compound $I_{6/a}$ DSC thermogram at a heating rate of 10 °C min$^{-1}$.

![POM images](image)

**Figure 3.** Nematic textures under POM on heating of the compound $I_{16/c}$ at (a) 130.0 °C and (b) 150.0 °C.
Table 1. Mesomorphic transition temperatures (T, °C), enthalpy (ΔH, kJ/mole) of transition, normalized entropy (ΔS_{Nematic-Iso}/R) of transition, and N temperature range, ΔT, for compounds I_{n/x}.

| Compound | X     | T_{Crystal-Nematic} | ΔH_{Crystal-Nematic} | T_{Nematic-Iso} | ΔH_{Nematic-Iso} | ΔS_{Nematic-Iso}/R | ΔT  |
|----------|-------|----------------------|----------------------|----------------|-----------------|--------------------|------|
| I_{6/a}  | -OCH₃ | 129.2                | 45.78                | 199.6          | 1.93            | 0.49               | 70.4 |
| I_{6/b}  | -F    | 114.1                | 39.35                | 154.1          | 1.19            | 0.34               | 40.0 |
| I_{16/a} | -OCH₃ | 87.00                | 36.38                | 119.7          | 2.36            | 0.72               | 32.7 |
| I_{16/c} | -Cl   | 107.1                | 36.96                | 158.4          | 2.30            | 0.64               | 51.3 |

Iso denotes isotropic liquid phase.

Figure 4. DSC transitions of the derivatives, I_{n/x}.

Table 1 also shows the normalized entropy changes, ΔS/R, in the investigated derivatives (I_{n/x}). The data revealed that the N–I transition entropy changes showed relatively lower values. The estimated entropy changes values are independent on alkoxy chain length [64,65]. Additionally, these results were agreement with previous reports [66–68]. The stereo configurations of the central naphthalene moiety and terminal polar groups played an important role in the predicted thermal parameters, which will be discussed in the computational section. Moreover, the thermal cis/trans isomerization of the azo group was an essential factor in the lower entropy changes observed, as documented in previous studies [65,69–71]. Moreover, due to their nematic nature, of the mesophase, they exhibited the lowest order mesophase.

3.2. Comparison of the Investigated Derivatives (I_{n/x}) with Previously Prepared Series

The location of lateral substitution strongly affects the mesomorphic behavior of LC materials. To evaluate the effect of the extra fused ring on the mesomorphic behavior on the mesogenic core of the molecule, an initial comparison is made between the derivatives (I_{n/x}) and their corresponding laterally neat homologues bearing the central benzene ring (II_{n/x}, Scheme 3) [58]. The homologues series II_{n/x} exhibiting dimorphic phases (SmA and N) depending on the length of terminal chain (n). The comparison indicated that the incorporation of the extra fused ring in the central core disrupted smectic A molecular packing and gave only resulted in the N mesophase. A second comparison is then made
between the present compounds ($I_{n/x}$) and their corresponding isomers bearing the central benzene ring ($III_{x/n}$, Scheme 3) [57]. The homologues $III_{x/n}$ series were observed to have nematognomic phases with higher thermal stabilities than the present investigated series $I_{n/x}$. The results revealed that the positional exchange of azo/ester linkages decreased the thermal stability of the formed mesophases.

![Molecular structures of series $II_{n/x}$ and $III_{x/n}$](image)

**Scheme 3.** Molecular structures of series $II_{n/x}$ and $III_{x/n}$.

### 3.3. Geometrical Structures and DFT Investigations

Computational calculations were carried out for all synthesized central naphthyl derivatives ($I_{n/x}$) via the DFT method to correlate the predicted quantum chemical parameters and the experimental data. The DFT calculations were performed in the gas phase with a DFT/B3LYP program at a 6-311G** basis set. The prepared materials ($I_{n/x}$) displayed a mesomorphic behavior, this confirming their existence in a planar conformation. Figure 5 represents the optimized geometrical structure of each compound confirmed to be stable by frequency calculation; no imaginary frequency was predicted for any member. The zero-point energy and other calculated quantum thermal parameters are summarized in Tables 2 and 3. It can be seen from Figure 5 that all designed compounds were linear and planar. Additionally, the length of the terminal alkoxy chains had no significant effect on the planarity of the aromatic rings. It was found that, in [72], the planarity of the mesogenic cores planarity of the LC compounds was influenced by the mesomeric nature of the attached polar group. Hence, the conjugated $\pi$-cloud interactions resulting from the terminal polar substituents offered high thermal N stability and range with suitable geometrical parameters in the investigated derivatives. On the other hand, the zero-point energy and other calculated thermodynamic parameters listed in Table 2 depend on the nature of terminal substituent $X$. They were predicted to increase with the increasing the electron-donating mesomeric nature.
Figure 5. Optimum structures for molecules of the derivatives $I_{n/x}$, calculated at a B3LYP/6–311G** level.

Table 2. Thermal parameters at 25 °C calculated using the B3LYP/6–311G** method.

| Comp. | ZPE (Kcal/Mol) | Thermal Energy (Kcal/Mol) | Enthalpy (Kcal/Mol) | Gibbs Free Energy (Kcal/Mol) | Entropy (Cal Mol/k) |
|-------|-----------------|---------------------------|---------------------|----------------------------|--------------------|
| $I_{6/a}$ | 339.142 | 359.971 | 360.563 | 294.367 | 222.023 |
| $I_{6/b}$ | 313.606 | 333.312 | 333.905 | 270.090 | 214.037 |
| $I_{16/a}$ | 518.170 | 547.563 | 548.155 | 460.300 | 294.671 |
| $I_{16/c}$ | 491.790 | 520.310 | 520.903 | 434.582 | 289.519 |

Table 3. Total energy (H), $E_{\text{HOMO}}$ (ev), $E_{\text{LUMO}}$ (ev), $\Delta$E (ev), dipole moment (D), ionization energy (ev), electron affinity (ev), and polarizability (Bohr's) calculated using B3LYP/6–311G** method for the series $I_{n/x}$ homologues.

| Comp. | Total Energy (Hartree) | $E_{\text{HOMO}}$ (ev) | $E_{\text{LUMO}}$ (ev) | $\Delta$E (ev) | Dipole Moment (Debye) | IE (ev) | EA (ev) | Polarizability (Bohr's) |
|-------|----------------------|-----------------------|-----------------------|----------------|----------------------|---------|---------|------------------------|
| $I_{6/a}$ | -1570.995 | -5.632 | -2.439 | 3.193 | 1.7620 | 5.632 | 2.439 | 451.01 |
| $I_{6/b}$ | -1555.767 | -5.774 | -2.582 | 3.192 | 3.3197 | 5.774 | 2.582 | 424.69 |
| $I_{16/a}$ | -1963.817 | -5.627 | -2.439 | 3.188 | 1.6794 | 5.627 | 2.439 | 571.88 |
| $I_{16/c}$ | -2308.947 | -5.791 | -2.614 | 3.177 | 3.7771 | 5.791 | 2.614 | 561.58 |

Abbreviations: $E_{\text{HOMO}}$ denotes to the energy of the highest occupied molecular orbital, $E_{\text{LUMO}}$ denotes to the energy of the lowest unoccupied molecular orbital and $\Delta$E = $E_{\text{LUMO}}$–$E_{\text{HOMO}}$ the orbital energy gap.
As can be seen in Table 3, the calculated ionization potentials (IE) for the terminal methoxy compounds (I\textsubscript{6/a} and I\textsubscript{16/a}) have lower values, which indicate that they are more basic than other electron-withdrawing derivatives [73]. Moreover, the predicted polarizability listed in Table 3 decreased in the order of I\textsubscript{16/a} > I\textsubscript{16/c} > I\textsubscript{6/a} > I\textsubscript{6/b}, showing that the changing values may be attributed to the aspect ratio of each molecule. As the molecular structure aspect ratio increased, the space filling of the mesomorphic compound also increased, resulting in enhanced polarizability. In general, lateral and terminal substituent polarity, polarizability, rigidity, and the shape of the liquid crystalline molecules are essential parameters for forming mesophases of specific types and thermal stabilities. The results in Table 3 also showed that the longer terminal chain derivatives (I\textsubscript{16/a} and I\textsubscript{16/c}) had lower values of predicted total energy (−1963.82 and −2308.95 Hartree). Thus, the terminal aggregation strength increased along with the length of the alkoxy chain, but with a decrease in total thermodynamic energy. It was reported that [64,65], the terminals of the chains always change their conformation dynamically and are randomly pointed out within the chain-layer. The random packing of the chains results in the loss of the two-dimensional symmetry within the chain-layer.

4. Conclusions

Four new mesomorphic derivatives based on an extra laterally fused ring in the central of a molecule, namely 4-((4-(alkoxy)phenyl)diazenyl)naphthalen-1-yl 4-substitutedbenzoate (I\textsubscript{n/x}), were synthesized and mesomorphically investigated, as well as theoretically evaluated. Molecular structure elucidation was carried out by elemental analyses and FTIR and NMR spectroscopy. Mesomorphic examinations of the prepared compounds were measured via DSC and POM. Evaluations of the DSC and POM investigations revealed that all the laterally substituted derivatives synthesized were enantiotropic, exhibiting a purely nematic mesophase with high thermal stability and a broad range. The size and mesomorphic effects of different terminal polar groups (CH\textsubscript{3}O, F, Cl) participated in the stabilization of the molecule, which achieved higher thermal N stability than the corresponding previously reported molecules. Computational DFT calculations indicated that the rigidity of the molecule increased after the extra fused ring was attached in the center of the structural shape, thus affecting the thermal and geometrical parameters. Moreover, the predicted energy gaps confirmed that the I\textsubscript{16/c} derivative was more reactive than the other compounds.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma14102587/s1. The synthetic and characterization details of investigated compounds.
1. Materials; 2. Synthesis of 4-((4-(alkoxy)phenyl)diazenyl)naphthalen-1-yl 4-substitutedbenzoate (I\textsubscript{n/x}); 3. Synthesis of 4-((4-(alkoxy)phenyl)diazenyl)naphthalen-1-yl 4-substitutedbenzoate In/x; 4. Characterization; 5. Computational Method.

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