DFT Calculations and Mesophase Study of Coumarin Esters and Its Azoesters

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Abstract: Two groups of coumarin derivatives, 4-methyl-2-oxo-2H-chromen-7-yl 4-alkoxybenzoates (coumarin esters), I\textsubscript{n}, and 4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-alkoxyphenyl)diazenyl) benzoates (coumarin azoesters), II\textsubscript{n}, were synthesized and investigated for their mesophase behavior and stability. Each group constitutes five series that differ from each other by length of the mesogenic part. Within each homologous series, the length of the terminal alkoxy group varies between 6, 8, 10, 12 and 16 carbons. Mesophase behavior was investigated by differential scanning calorimetry (DSC) and identified by polarized light microscopy (PLM). Density functional theory (DFT) calculations for coumarin derivatives were discussed. The results revealed that the incorporation of azo group incorporated in the mesogenic core decreases the energy differences, increases the dipole moments and stabilities of coumarin azoesters series more than coumarin esters.

Keywords: liquid crystal; coumarin derivatives; non-mesomorphic; mesophase stability; DFT calculations

1. Introduction

Coumarin derivatives display excellent kinds of photochemical and photophysical properties. They become useful in different applications like brightening agents [1] and organic light-emitting diodes (LED) [2–4]. Moreover, they exhibit an excellent and wide range of biological activity, such as antibiotic, anticancer, antifungal, ant-coagulating, anti-inflammatory, plant growth regulating agents and analytical reagents [5–7]. Additionally, polymeric and non-polymeric coumarin derivatives display liquid-crystalline properties [8–11]. Thus, coumarins have become an interesting molecular framework to be incorporated in numerous electronic organic materials, with potential applications in OLED, solar cells and photo alignment technologies for liquid crystal displays [12,13]. Mesophase stability of an organic compound depends primarily on its molecular architecture in which a slight change in the molecular geometry enables considerable change in its mesomorphic properties [14,15]. Generally, the stability of the mesophase is increased as the polarity and/or polarizability of the central part of the molecule increase. Mesomorphic properties of nematic mesogens are strongly impacted by the lateral group. The degree of such impact is dependent on the size, position, and polarity of the lateral substituent. Sterically, a lateral substituent effectively widens the core and increases the intermolecular separation. This leads to a reduction in lateral interactions [16–18] and, hence, the nematic stability is reduced. Gray [19] has clarified that an increase in the breadth of the molecules reduces the stability of both the nematic and smectic mesophases. High demand for new liquid crystals for applications has led to the preparation and study of numerous mesogens, particularly thermotropic liquid crystals [14,15].
Most thermotropic liquid crystals are rod-like molecules having a rigid core composed of two or more phenyl rings and one or more flexible terminal alkyl chains. Coumarin derivatives have readily available electrons that enable the photo-excitation of the dye to an excited state. Due to this attractive structure-property relationship, coumarins allow the synthesis of suitable dyes with appropriate groups by either adding chromophore groups or expanding the \( \pi \) system (a conjugation path) between them. Connecting theoretical calculations of molecular structure with experimental data is one of our interests [20–23]. In liquid crystals, the molecular structures as well as the interactions between the molecules have large effects on their physical properties [24–27].

The mesomorphic properties of nematic mesogens are strongly influenced by a lateral group appended to a nematic core. The extent of such effect is dependent on the size, position, and polarity of the lateral substituent. A large lateral substituent effectively widens the core and increases the intermolecular separation, and this reduces nematic stability by a reduction of the lateral interactions [16–18]. Furthermore, Gray [19] reported that an increase in the breadth of the molecules reduces the stability of both the nematic and smectic mesophases.

In the present work, in order to obtain a further understanding of the structure-property relationship of liquid crystalline compounds having coumarin derivatives, two series of lateral methyl coumarin esters, \( I_n \), and coumarin azoesters \( II_n \), have been synthesized and investigated in terms of their mesophase behavior as well as DFT calculation to illustrate the effect of the length of the alkoxy chain as well as the mesogenic part on their mesophase stability (Figure 1).

![Figure 1. Prepared compounds \( I_n \) and \( II_n \).](image)

2. Experimental

2.1. Materials

Hexyl bromide, octyl bromide, decyl bromide, dodecyl bromide and hexadecyl bromide were obtained from Sigma Aldrich (Darmstadt, Germany). Phenol, \( p \)-aminobezoic acid, 4-n-hexyoxyl...
benzoic acid, 4-n-octyloxy benzoic acid, 4-n-decyloxy benzoic acid and 4-n-dodecyloxy benzoic acid were obtained from Merck (Darmstadt, Germany). N,N’-dicyclohexylcarbodiimide (DCC), tributylammoniumbromide (TBAB) and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Missouri, WI, USA). Dichloromethane, ethanol and methanol were of pure grade and purchased Aldrich (Missouri, WI, USA).

2.2. Synthesis of Coumarin Derivatives

Coumarin esters, I, and coumarin azoesters II, were synthesized according to the following Scheme 1:

\[ \text{Scheme 1. Synthesis of coumarin derivatives } \text{I} \text{ and } \text{II}. \]

2.2.1. Synthesis of 4-methyl-2-oxo-2H-chromen-7-yl 4-alkoxybenzoate, I

To a mixture of the 7-hydroxy-4-methyl-2H-chromen-2-one (0.01 mole) and 0.01 mole of 4-alkoxybenzoic acid in 25 mL dry methylene chloride N,N’-dicyclohexylcarbodiimide (DCC, 0.02 mole) and few crystals of 4-dimethylaminopyridine (DMAP) were added. The reaction mixture was stirred for 72 h at room temperature. The separated precipitate was filtered off and the filtrate was evaporated. The solid residue obtained was recrystallized from ethanol.

4-methyl-2-oxo-2H-chromen-7-yl 4-hexyloxybenzoate I₆.

Yield: 89.2%; mp. 110.0 °C, FTIR (υ, cm⁻¹): 2923, 2856 (CH₂ stretching), 1722 (C=O), 1625 (C=N), 1605 (C=C), 1469 (C−O Asym), 1245 (C−O Sym). Elemental analyses: C₂₃H₂₄O₅ Found (Calc.): C, 72.21 (72.61); H, 6.29 (6.36).
4-methyl-2-oxo-2H-chromen-7-yl 4-octyloxybenzoate I₈.

Yield: 91.3%; mp. 104.0 °C, FTIR (ν, cm⁻¹): 2919, 2846 (CH₂ stretching), 1724 (C=O), 1624 (C=N), 1604 (C=C), 1467 (C=O Asym), 1253 (C=O Sym). Elemental analyses: C₂₅H₂₈O₅ Found (Calc.): C, 73.39 (73.51); H, 6.88 (6.91).

4-methyl-2-oxo-2H-chromen-7-yl 4-decyloxybenzoate I₁₀

Yield: 93.8%; mp. 108.0 °C, FTIR (ν, cm⁻¹): 2921, 2851 (CH₂ stretching), 1726 (C=O), 1626 (C=N), 1604 (C=C), 1469 (C=O Asym), 1247 (C=O Sym). Elemental analyses: Found (Calc.): C₂₇H₃₂O₅ C, 74.33 (74.29); H, 7.45 (7.39).

4-methyl-2-oxo-2H-chromen-7-yl 4-dodecyloxybenzoate I₁₂

Yield: 90.7%; mp 107.0 °C, FTIR (ν, cm⁻¹): 2921, 2850 (CH₂ stretching), 1726 (C=O), 1625 (C=N), 1604 (C=C), 1469 (C=O Asym), 1247 (C=O Sym). Elemental analyses: Found (Calc.): C₂₉H₃₆O₅ C, 74.75 (74.97); H, 7.64 (7.81).

4-methyl-2-oxo-2H-chromen-7-yl 4-hexadecyloxybenzoate I₁₆

Yield: 90.9%; mp. 109.0 °C, FTIR (ν, cm⁻¹): 2919, 2850 (CH₂ stretching), 1726 (C=O), 1626 (C=N), 1604 (C=C), 1470 (C=O Asym), 1247 (C=O Sym). Elemental analyses: C₃₅H₄₄O₅ Found (Calc.): C, 76.01 (76.12); H, 8.33 (8.52).

2.2.2. Synthesis of 4-(2-(4-alkoxyphenyldiazenyl)benzoic acid

A mixture of 4-(2-(4-hydroxyphenyldiazenyl)benzoic acid (5.0 mmol), alkylbromide (6.0 mmol), tetrabutylammonium bromide (0.17 g, 0.50 mmol), and potassium hydroxide (0.11 g, 2.0 mmol) was heated under reflux for 6 h. After cooling, the reaction mixture was neutralized with 4N HCl and extracted with methylene chloride (3 × 20 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and the solvent was evaporated to dryness. The products were purified by recrystallization by aqueous ethanol (1:1).

2.2.3. Synthesis of 4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-alkoxyphenyldiazenyl)benzoate, IIₙ

N,N′-dicyclohexylcarbodiimide (DCC, 0.02 mole) and few crystals of 4-dimethylaminopyridine (DMAP) were added to a mixture of the 7-hydroxy-4-methyl-2H-chromen-2-one (0.01 mole) and 0.01 mole of 4-(2-(4-alkoxyphenyldiazenyl)benzoic acid in 25 mL dry methylene chloride. The reaction mixture was stirred for 72 h at room temperature. The separated dicyclohexylurea (DCU) was filtered off and the filtrate was evaporated. The solid residue obtained was recrystallized from ethanol.

4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-hexyloxyphenyldiazenyl)benzoate II₆

Yield: 92.3%; mp 122.7 °C, FTIR (ν, cm⁻¹): 2928, 2856 (CH₂ stretching), 1726 (C=O), 1602 (C=C), 1498 (C=O Asym), 1245 (C=O Sym). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 0.92 (t, 3H, CH₃(CH₂)₃CH₂CH₂O, J = 6.6 Hz), 1.15–1.36 (m, 6H, CH₃(CH₂)₃CH₂CH₂O), 1.76–1.85 (m, 2H, CH₃(CH₂)₃CH₂CH₂O), 2.47 (s, 3H, CH₃), 4.07 (t, 2H, CH₃(CH₂)₃CH₂CH₂O, J = 6.4 Hz), 6.31 (s, 1H, Ar–H) 7.00–7.04 (m, 2H, Ar–H), 7.24–7.29 (m, 2H, Ar–H), 7.66–7.69 (m, 2H, Ar–H), 7.89–8.00 (m, 3H, Ar–H), 8.33 (d, 2H, J = 8.7 Hz, Ar–H). ¹³C NMR (101 MHz, CDCl₃) δ = 164.04, 162.50, 160.43, 155.99, 154.17, 153.36, 152.02, 146.85, 131.40, 129.60, 127.61, 125.49, 125.13, 122.65, 118.27, 117.97, 114.87, 110.69, 68.50, 32.36, 29.14, 25.70, 22.61, 18.80, 14.05. Elemental analyses: C₂₉H₂₈N₂O₅ Found (Calc.): C, 72.15 (71.88); H, 5.99 (5.82); N, 5.49 (5.78).

4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-octyloxyphenyldiazenyl)benzoate II₈

Yield: 91.7%; mp 107.5 °C, FTIR (ν, cm⁻¹): 2925, 2855 (CH₂ stretching), 1726 (C=O), 1603 (C=C), 1499 (C=O Asym), 1246 (C=O Sym). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 0.91 (t, 3H, CH₃(CH₂)₃CH₂CH₂O, J = 6.6 Hz), 1.12–1.39 (m, 10H, CH₃(CH₂)₃CH₂CH₂O), 1.69–1.82 (m, 2H, CH₃(CH₂)₃CH₂CH₂O), 2.45
(s, 3H, CH₃), 4.05 (t, 2H, CH₂(4H₂)₃CH₂CH₂O, J = 6.5 Hz), 6.31 (s, 1H, Ar–H) 7.00–7.04 (m, 2H, Ar–H), 7.21–7.31 (m, 2H, Ar–H), 7.62–7.67 (m, 2H, Ar–H), 7.92–8.02 (m, 3H, Ar–H), 8.33 (d, 2H, J = 8.8 Hz, Ar–H). Elemental analyses: C₃₅H₃₂N₂O₅ Found (Calc.): C, 72.45 (72.64); H, 6.01 (6.29); N, 5.12 (5.47).

4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-decyloxyphenyl)diazenyl)benzoate II₀

Yield: 88.9%; mp 137.5 °C, FTIR (ν, cm⁻¹): 2926, 2853 (CH₂ stretching), 1724 (C=O), 1605 (C=O), 1497 (C=O, Asym), 1248 (C=O, Sym). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 0.89 (t, 3H, CH₃(CH₂)₃CH₂CH₂O, J = 6.9 Hz), 1.08–1.41 (m, 14H, CH₂(4H₂)₃CH₂CH₂O), 1.79–1.88 (m, 2H, CH₂(4H₂)₃CH₂CH₂O), 2.44 (s, 3H, CH₃), 4.09 (t, 2H, CH₂(4H₂)₃CH₂CH₂O, J = 6.5 Hz), 6.31 (s, 1H, Ar–H) 7.00–7.04 (m, 2H, Ar–H), 7.23–7.30 (m, 2H, Ar–H), 7.60–7.68 (m, 2H, Ar–H), 7.91–8.02 (m, 3H, Ar–H), 8.34 (d, 2H, J = 8.8 Hz, Ar–H). Elemental analyses: C₃₃H₃₂N₂O₅ Found (Calc.): C, 73.03 (73.31); H, 6.35 (6.71); N, 4.75 (5.18).

4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-dodecyloxyphenyl)diazenyl)benzoate II₁₀

Yield: 92.2%; mp 131.0 °C, FTIR (ν, cm⁻¹): 2918, 2851 (CH₂ stretching), 1727 (C=O), 1603 (C=O), 1498 (C=O, Asym), 1244 (C=O, Sym). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 0.88 (t, 3H, CH₃(CH₂)₃CH₂CH₂O, J = 6.5 Hz), 1.21–1.57 (m, 6H, CH₃(CH₂)₃CH₂CH₂O), 1.80–1.87 (m, 2H, CH₂(4H₂)₃CH₂CH₂O), 2.47 (s, 3H, CH₃), 4.08 (t, 2H, CH₂(4H₂)₃CH₂CH₂O, J = 6.4 Hz), 6.31 (s, 1H, Ar–H) 7.04 (d, 2H, J = 8.4 Hz, Ar–H), 7.24–7.29 (m, 2H, Ar–H), 7.70 (d, 2H, J = 8.4 Hz, Ar–H), 7.89–8.00 (m, 3H, Ar–H), 8.35 (d, 2H, J = 8.7 Hz, Ar–H). ¹³C NMR (101 MHz, CDCl₃) δ = 164.15, 162.61, 160.54, 156.09, 154.30, 153.36, 151.94, 146.86, 131.40, 129.59, 125.49, 125.39, 122.64, 118.26, 118.02, 114.87, 114.65, 110.69, 68.50, 31.93, 29.68, 29.65, 29.61, 29.58, 29.39, 29.37, 29.17, 26.02, 22.71, 18.80, 14.14. Elemental analyses: C₃₅H₄₆N₂O₅ Found (Calc.): C, 73.79 (73.92); H, 6.61 (7.09); N, 4.49 (4.93).

4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-dodecyloxyphenyl)diazenyl)benzoate II₁₂

Yield: 90.1%; mp 126.0 °C, FTIR (ν, cm⁻¹): 2918, 2849 (CH₂ stretching), 1726 (C=O), 1602 (C=O), 1501 (C=O, Asym), 1246 (C=O, Sym). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 0.91 (t, 3H, CH₃(CH₂)₃CH₂CH₂O, J = 6.5 Hz), 1.21–1.83 (m, 6H, CH₃(CH₂)₃CH₂CH₂O), 2.46 (s, 3H, CH₃), 4.06 (t, 2H, CH₂(4H₂)₃CH₂CH₂O, J = 6.8 Hz), 6.31 (s, 1H, Ar–H) 7.04 (d, 2H, J = 8.4 Hz, Ar–H), 7.24–7.29 (m, 2H, Ar–H), 7.70 (d, 2H, J = 8.4 Hz, Ar–H), 7.89–8.00 (m, 3H, Ar–H), 8.35 (d, 2H, J = 8.8 Hz, Ar–H). Elemental analyses: C₃₉H₄₈N₂O₅ Found (Calc.): C, 74.68 (74.97); H, 7.63 (7.74); N, 4.39 (4.48).

2.3. Characterization

The purity of the prepared samples was checked with thin-layer chromatography (TLC) using TLC sheets coated with silica gel (E Merck), and CH₂Cl₂/CH₃OH (9:1) as eluent, whereby only one spot was detected by a UV-lamp.

Infrared spectra were recorded using Perkin-Elmer B25 spectrophotometer (Perkin-Elmer, Inc., Shelton, CT USA). ¹H NMR spectra were performed using a Varian EM 350 L 300 MHz spectrometer (Varian, Oxford, UK) using tetramethylsilane as internal standard and CDCl₃ as solvent; the chemical shift values recorded as δ (ppm units). Elemental analyses for final products were carried out on Thermo Scientific Flash 2000 CHS/O Elemental Analyzer, Milan, Italy.

Calorimetric measurements were carried out using a TA Instruments Co. Q20 Differential Scanning Calorimeter (TA Instruments Co. Q20, DSC, New Castle, DE USA). The DSC was calibrated using the melting temperature and enthalpy of indium and lead. DSC investigation was carried out for small samples (2–3 mg) placed in aluminum pans. All measurements were achieved at a heating rate of 10 °C/min in inert atmosphere of nitrogen gas (30 mL/min) and all transition recorded from the second heating scan.

Transition temperatures were checked and types of mesophases identified, for all compounds prepared, with a standard polarized light microscope (PLM, Wild, Germany) attached with Mettler FP82HT hot stage.
2.4. Methods and Calculations

All calculations for the studied coumarin derivatives were carried out using Gaussian 09 software (version 09) [28] on a Pentium IV processor personal computer. The calculations were performed by DFT/B3LYP methods using 6-31G (d,p) basis set. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. Gauss View [29] has been used to draw the structures of the optimized geometries. Also, frequency calculations were performed using the same level of theory. The frequency calculations showed that all structures were stationary points in the geometry optimization procedures and none showed imaginary frequencies in the vibrational analyses. Vibrational mode assignments were made by visual inspection of the modes animated by using Gauss View program.

3. Results and Discussion

3.1. Infrared Absorption Spectra of Components (Iₙ)

Infrared spectra observed for the all compounds Iₙ and IIₙ under investigation showed no significant effect of the length of the alkoxy chain on the position of FTIR absorption bands of the main characteristic functional groups.

3.2. Mesophase Behavior of the Investigated Coumarin Derivatives

Transition temperatures and transition enthalpies as measured by DSC, and the phases identified by polarized light microscopy PLM, for synthesized derivatives coumarinesters, Iₙ, and coumarinazaoesters, IIₙ, are summarized in Table 1. DSC curves for I₈ and II₁₀ upon heating and cooling are depicted in Figure 2 as representative examples. The effect of increasing alkoxy-chain length on the mesophase behavior of compounds in series Iₙ is represented graphically in Figure 3a and those of coumarinazaoesters IIₙ, for comparison, are depicted in Figure 3b.

The data in Table 1 and Figure 3 reveal that all coumarinesters, Iₙ, series are non-mesomorphic. Conversely, all compounds in Coumarin azoesters group IIₙ are enantiotropically mesomorphic, these results are consistent with previous finding [30]. All members of group IIₙ are dimorphic exhibit smectic C (SmC) and nematic phases (N) except II₁₆ is monomophic showing only SmC phase. Phases were confirmed by the miscibility method, using 4-hexadecyloxybenzoic acid as the mesophase reference. Generally, the stability of the mesophase is augmented by an increase in the polarity and/or polarizability of the mesogenic part of the molecule. It was found that [19], the stability and types of the mesophase produced are dependent on the dipole moment of the mesogenic core, and that coumarinazaoesters (IIₙ) homologues are mesomorphic with high stability.

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Abbreviations: T_cr-SmC = crystal to smectic C phase transition; T_smC-N = smectic C to Nematic transition; T_SmC-I = smectic C to isotropic liquid transition; T_N-I = Nematic to isotropic liquid transition; ΔH_cr-SmC = crystal to smectic C phase transition; ΔH_smC-N = smectic C to Nematic transition; ΔH_SmC-I = smectic C to isotropic liquid transition; ΔH_smC-N/R = smectic C to Nematic transition entropy; ΔS_smC-N/R = Nematic to isotropic liquid transition entropy.
Figure 2. DSC thermograms of some representative compounds recorded from heating and cooling at a rate of 10 °C/min for: (a) I4 and (b) II1b.

Figure 3b shows that the nematic-to-isotropic transition temperatures \( T_{N-I} \) decrease gradually with the increase of the alkoxy-chain length (n). This trend is in accordance with that shown by Gray [19] and Imrie and Taylor [31] in which the nematic-to-isotropic transition temperatures fall with increasing alkoxy-chain length, and also for the smectic phase, the smectic-nematic, or smectic-to-isotropic transition temperatures rise gradually as the alkoxy chain lengthens.

The mesophase behavior of a calamitic mesogen is affected by the molecular–molecular interactions that depend mainly on geometry of the molecules, polarizability anisotropy of the core molecule, as well as the stereo electronic properties of the whole molecule. Therefore, in the present studied coumarin derivatives, molecular association of the rod-like molecules, and consequently their mesophases stability \( T_c \) depends mainly on lateral adhesion of linear molecules that increases with the increase of the alkoxy-chain length (n). However, the increased alkyl-chain length reduces the rod-shaped molecule’s rigidity and, consequently, its ability to fit readily into the parallel arrangement within the nematic phase. As a result, nematic phase stability decreases with increasing the alkoxy chain length. The end-to-end intermolecular interactions play a role in determining the SmC-to-isotropic transition temperatures, that is, the construction of the smectic molecular order is determined by the fact that the terminal attractions become stronger, allowing the arrangement of the layers to occur more easily as the alkoxy chains increased, which in turn enhances the SmC-to-I transition.

When the present investigated coumarin azoesters are compared with coumarin esters for the corresponding alkoxy chain length, it is found that incorporation of phenyl azo group to the coumarin ester derivatives led to an increase in the polarizability of the whole compound and consequently enhanced the intermolecular association between molecules.

Normalized entropies of the smectic C-nematic \( \Delta S_{\text{SmC-N}/R} \) and nematic-isotropic \( \Delta S_{\text{N-I}/R} \) transitions for coumarinazoesters derivatives were calculated and appended to Table 1. Entropies of N–I transitions \( \Delta S_{\text{N-I}/R} \) are of lower values than those of the corresponding \( \Delta S_{\text{SmC-N}/R} \) transitions. The decrease observed in \( \Delta S_{\text{N-I}/R} \) was presumably in part a reflection of the increase in the biaxiality of the mesogenic group, resulted from the flexible terminal alkoxy-chain, being less strongly anchored at its end, giving a resulting decrease in conformational entropy [32].
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3.3. Stabilities, Total Energies, Dipole Moments

Since the mesophase stability of liquid crystalline compounds is dependent upon the intermolecular attractions, in which molecular polarity plays a significant role, it has been shown [33] that in a series of compounds the dipole moment of any compound is dependent upon the nature of the substituent. It has also been shown [34,35] that the dipole moments of all members of a homologous series are virtually the same irrespective of the alkoxy-chain length. The calculated total energies, dipole moments of the studied compounds are summarized in Table 2. The optimized structures of I6 and II6 shown in Figure 4 were calculated using 6-311G(d,p) level of theory.

Table 2. Total energies (a.u), dipole moments (Debye) using B3LYP/6-31G(d,p) method.

<table>
<thead>
<tr>
<th></th>
<th>I6</th>
<th>II6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole moment (Debye)</td>
<td>X</td>
<td>Y</td>
</tr>
<tr>
<td>Energy (a.u.)</td>
<td>3.98</td>
<td>−1.62</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
<td>−2.31</td>
<td>0.03</td>
</tr>
<tr>
<td>Energy (a.u.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 3](image-url) Effect of alkoxy-chain length on the mesophase behavior of the individual homologous series of (a) I6 and (b) II6.

![Figure 4](image-url) The optimized structures of I6 and II6.
The results of energy analysis showed that I_6 has energy $-1266.70$ a.u., while, II_6 has $-1607.11$ a.u. The high energy difference between the two compounds could be attributed to the extra conjugation of II_6 than the I_6 due to the attachment of the extra azo phenyl group in the mesogenic part, while, the dipole moment of II_6 is also more than that of I_6.

3.4. Molecular Electrostatic Potential (MEP)

The molecular electrostatic potentials of I_6 and II_6 are given in Figure 5. Many properties such as molecular polarizability, dipole moment and electronic structure are highly affected by the charge calculations at atomic sites of compounds under investigations [36]. Moreover, the molecular electrostatic potential (MEP) is a useful property to study the distribution of the electron density [37–39]. In MEPs, the red color is the region of maximum negative charges. The studied compounds have more electron deficient centers which mainly localized on the esters group either of benzoate or coumarin moieties, while the electron rich region is located on the methyl group of the coumarin part for both compounds. Also, the molecular electrostatic potential (MEP) is best suited for identifying the presence of intra- and intermolecular interactions on the different atomic sites.

Figure 5. Molecular Electrostatic potentials (MEP) mapped on the electron density surface calculated by the DFT/B3LYP method.

3.5. Frontier Molecular Orbitals

One of the important properties for chemists and physicist is the nature of the frontier molecular orbitals (FMOs), like energy level and electron densities. The location of electron densities of FMOs are used for calculation of the reactive position in the compounds under investigation [40].

LUMO is the lowest unoccupied molecular orbital and HOMO is the highest occupied molecular orbital, and their energy gap ($\Delta E$) shows the chemical reactivity of the molecule. The HOMO, LUMO and $\Delta E$ values of the studied compound were calculated by the B3LYP/6-311G(d,p) method. Where A molecule having high $\Delta E$ is less polarizable and is generally associated with a low chemical reactivity and high kinetic stability [41]. The HOMO and LUMO pictures are shown in Figure 6. As shown in Figure 6 for compound I_6, the electron densities of the HOMO and LUMO are mainly localized on the coumarin moiety, while that of II_6 HOMO and LUMO is located on the azo part. Moreover, attachment of the azo group in II_6 affords HOMO and LUMO with lower energy difference (0.12311) rather than that of I_6 (0.159128); it could be attributed to the extra conjugation of the azo part which decreases the
energy difference between the frontier molecular orbitals. This lower energy difference \( \Delta E \) makes it more polarizable than that of \( I_6 \).

![Figure 6. The ground state isodensity surface plots for the frontier molecular orbitals.](image)

4. Conclusions

Two groups of coumarin derivatives were synthesized and investigated for their mesophase behavior and stability. The study revealed that, irrespective of the length of the alkoxy chains, all compounds of the first group, 4-methyl-2-oxo-2H-chromen-7-yl 4-alkoxybenzoates, \( I_6 \) were found to be non-mesomorphic, while 4-methyl-2-oxo-2H-chromen-7-yl 4-(2-(4-alkoxyphenyl)diazeynil) benzoates, \( II_6 \), were dimorphic possessing SmC and nematic phases, except the compound \( II_{16} (n=16) \) is purely smectogenic has SmC phase. DFT calculations for coumarin derivatives were discussed and the result showed that the incorporation of azo group elongates the mesogenic core and hence decreases the energy differences between the FMOs and increases the dipole moments as well as the stabilities of coumarin azoesters series compared to coumarin esters.

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